Strong spin-orbit coupling effect induced large valley splitting in Janus MSeXH

(M = Cr, Mo, W; X = N, P)

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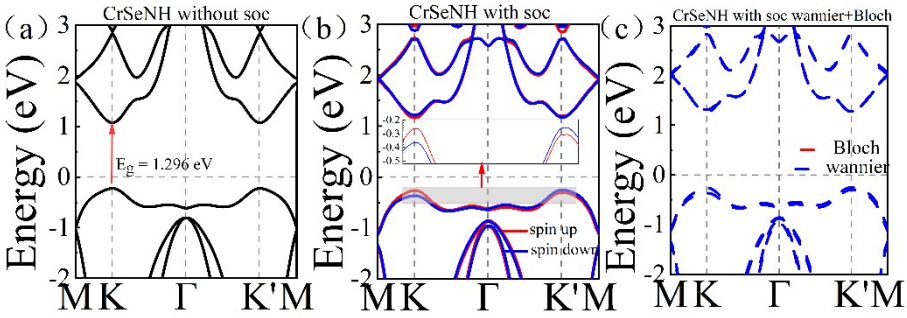
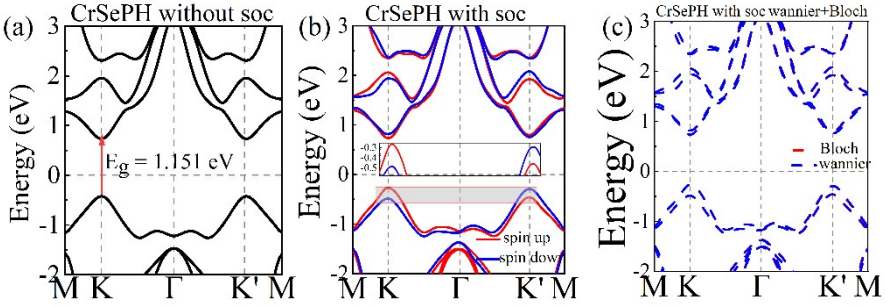
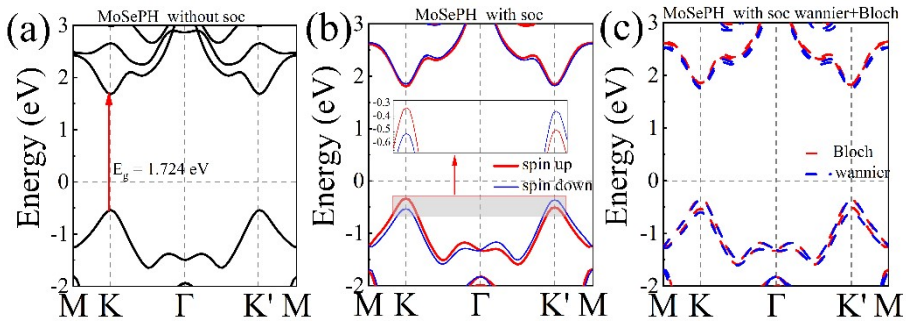


Support **Fig.1**: (a)The electron energy band diagram along the high symmetry points of CrSeNH without and (b)with considering *SOC*; (c) The red dashed line obtained from the Bloch, while the blue dashed line is derived from the Wannier functions with considering *SOC*. This figure is a superposition of the band structures from both methods and the Fermi energy is set to zero.



Support **Fig.2**: (a) The electron energy band diagram along the high symmetry points of CrSePH without and (b) with considering *SOC*, (c) The red dashed line obtained from the Bloch, while the blue dashed line derived from the Wannier functions with considering *SOC*. This figure is a superposition of the band structures from both methods and the Fermi energy is set to zero.



Support **Fig.3**: (a)The electron energy band diagram along the high symmetry points of MoSePH

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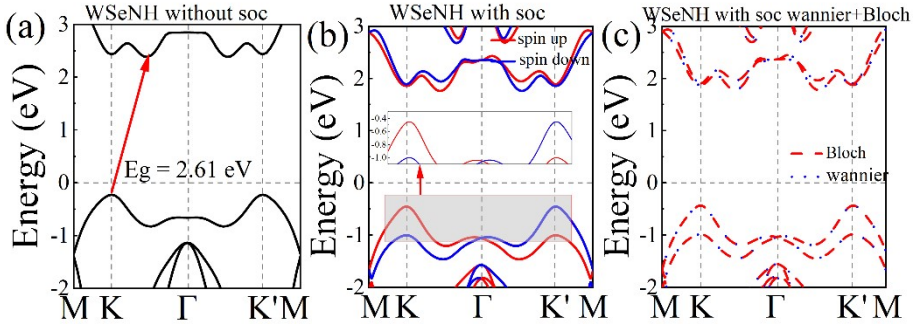
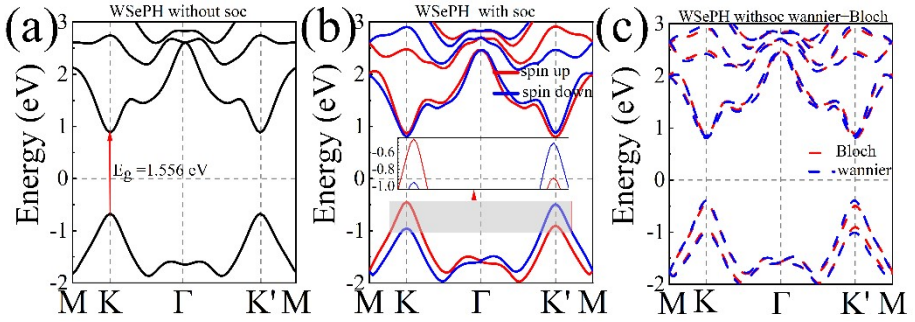
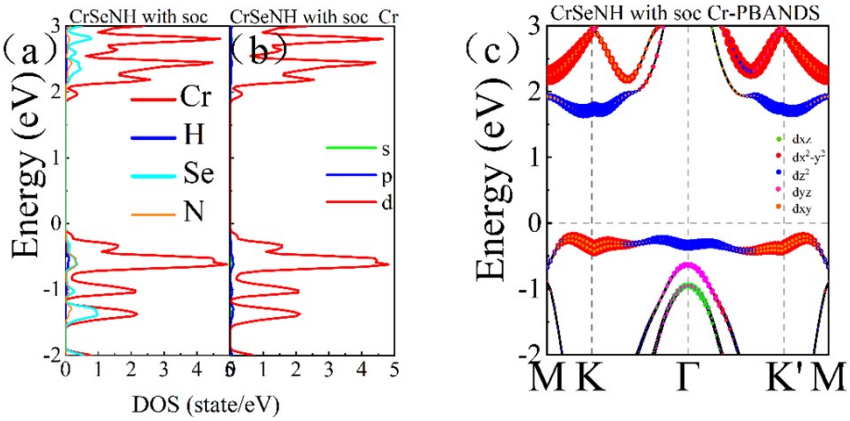
without and (b) with considering *SOC*; (c) The red dashed line obtained from the Bloch, while the blue dashed line derived from the Wannier functions with considering *SOC*. This figure is a superposition of the band structures from both methods and the Fermi energy is set to zero.



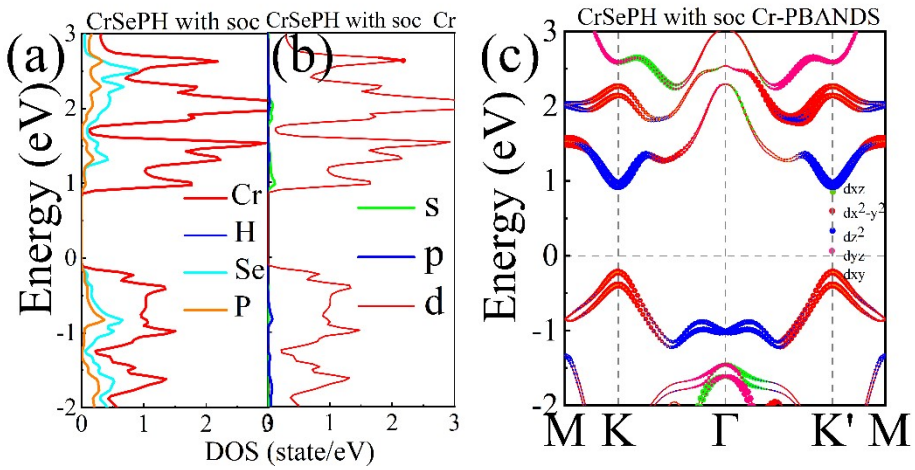
Support **Fig.4**: (a) The electron energy band diagram along the high symmetry points of WSeNH without and (b) with considering *SOC*, (c) The red dashed line obtained from the Bloch, while the blue dashed line derived from the Wannier functions with considering *SOC*. This figure is a superposition of the band structures from both methods and the Fermi energy is set to zero.



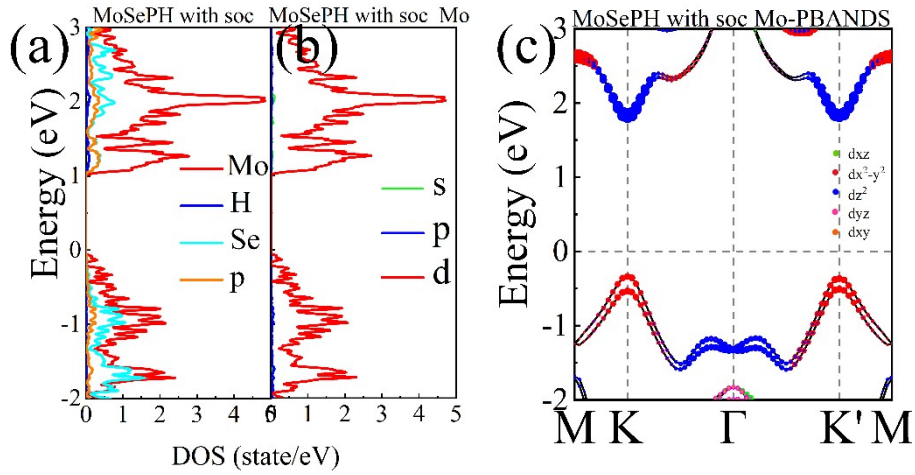
Support **Fig.5**: (a) The electron energy band diagram along the high symmetry points of WSePH without and (b) with considering *SOC*; (c) The red dashed line obtained from the Bloch, while the blue dashed line derived from the Wannier functions with considering *SOC*. This figure is a superposition of the band structures from both methods and the Fermi energy is set to zero.



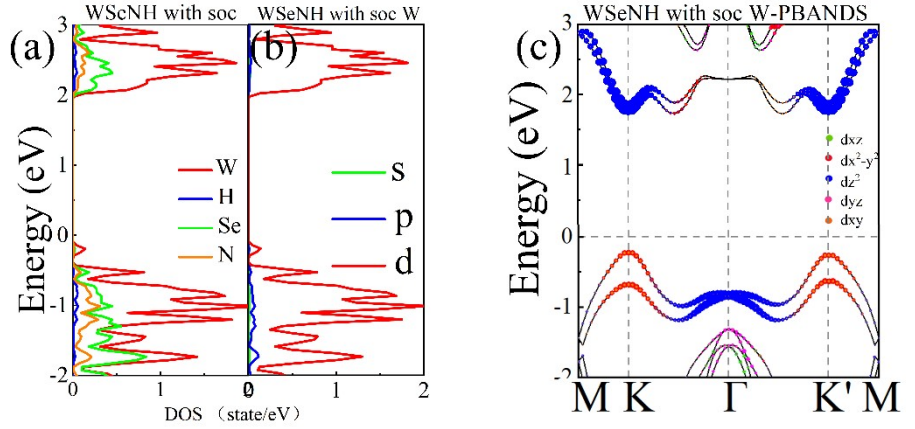
Support **Fig.6**: (a)The total density of states of each atom of 1L CrSeNH, (b) the projected density of states of the s, p, d orbitals of Cr atom, (c) The projected energy band diagram of the d orbitals of the Cr atom in two-dimensional, where the d_{xy}, d_{x2-y2}, d_{z2}, d_{yz}, d_{xz} orbitals of Cr is in green, red, blue, magenta, orange.



Support **Fig.7**: (a)The total density of states of each atom of 1L CrSePH, (b) the projected density of states of the s, p, d orbitals of Cr atom, (c) The projected energy band diagram of the d orbitals of the Cr atom in two-dimensional, where the d_{xy}, d_{x2-y2}, d_{z2}, d_{yz}, d_{xz} orbitals of Cr is in green, red, blue, magenta, orange.

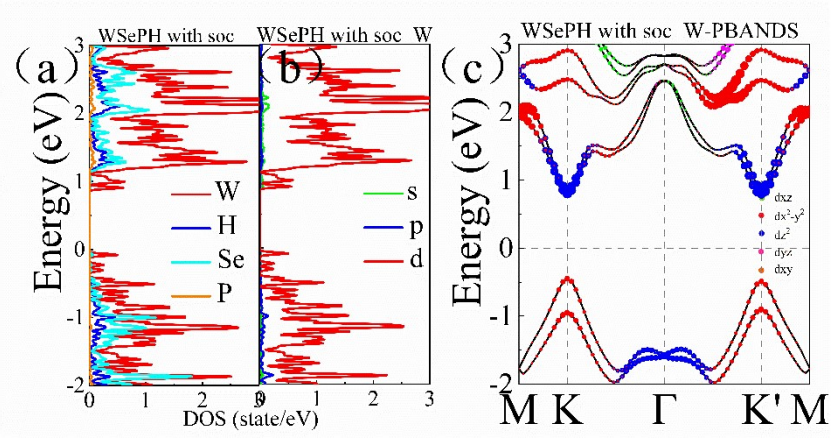


Support **Fig.8**: (a)The total density of states of each atom of 1L MoSePH, (b) the projected density of states of the s, p, d orbitals of Mo atom, (c) The projected energy band diagram of the d orbitals of the Mo atom in two-dimensional, where the d_{xy}, d_{x2-y2}, d_{z2}, d_{yz}, d_{xz} orbitals of Mo is in green, red, blue, magenta, orange.

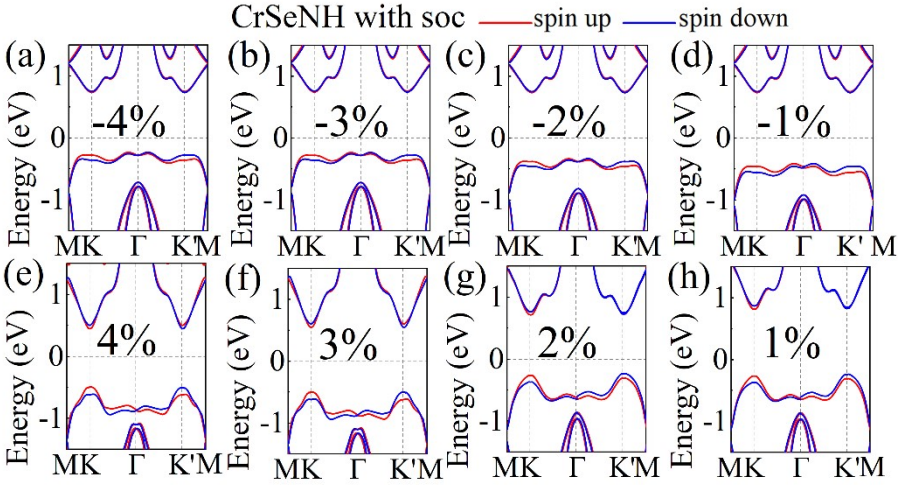


Support **Fig.9**: (a)The total density of states of each atom of 1L WSeNH, (b) the projected density of

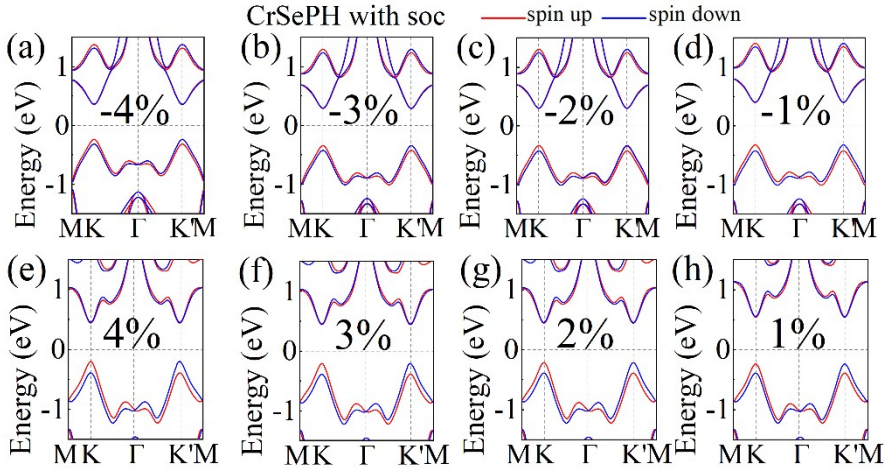
states of the s, p, d orbitals of W atoms, (c) The projected energy band diagram of the d orbitals of the W atom in two-dimensional, where the d_{xy}, d_{x2-y2}, d_{z2}, d_{yz}, d_{xz} orbitals of W is in green, red, blue, magenta, orange.



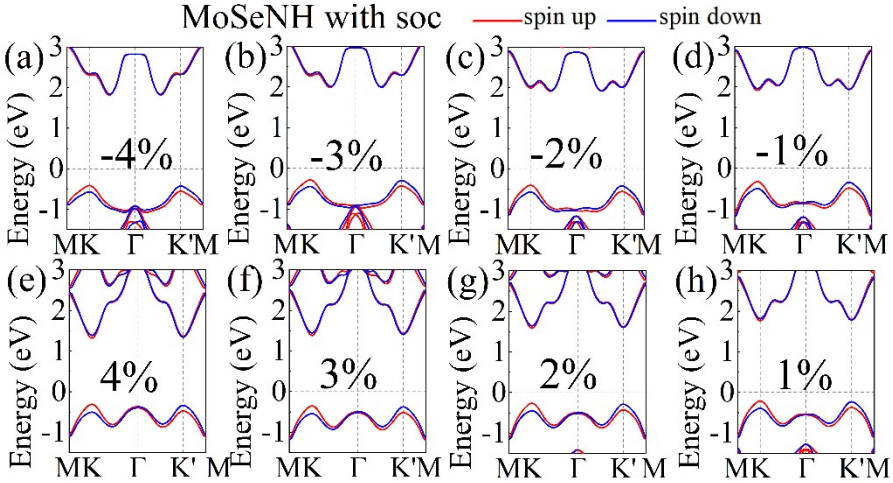
Support **Fig.10**: (a)The total density of states of each atom of 1L WSePH, (b) the projected density of states of the s, p, d orbitals of W atom, (c) The projected energy band diagram of the d orbitals of the W atom in two-dimensional, where the d_{xy}, d_{x2-y2}, d_{z2}, d_{yz}, d_{xz} orbitals of W is in green, red, blue, magenta, orange.



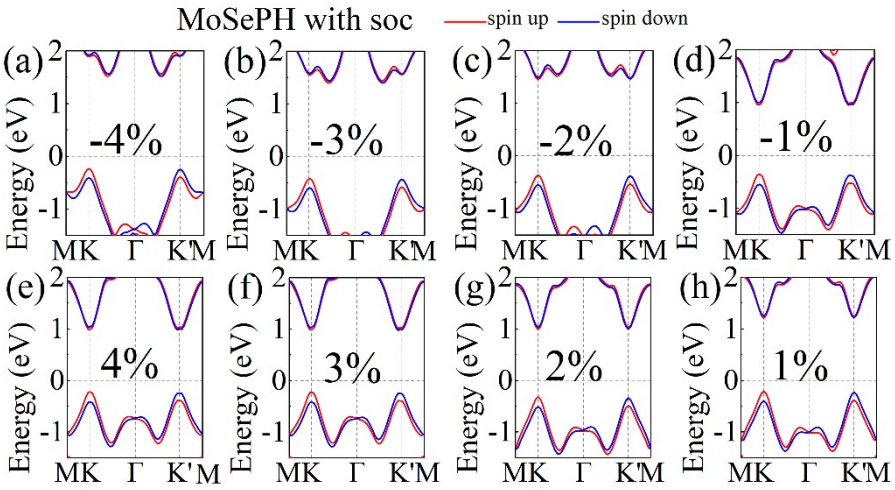
FigS11: (a-h) is a band plot at -4%-4% biaxial strain of CrSeNH.



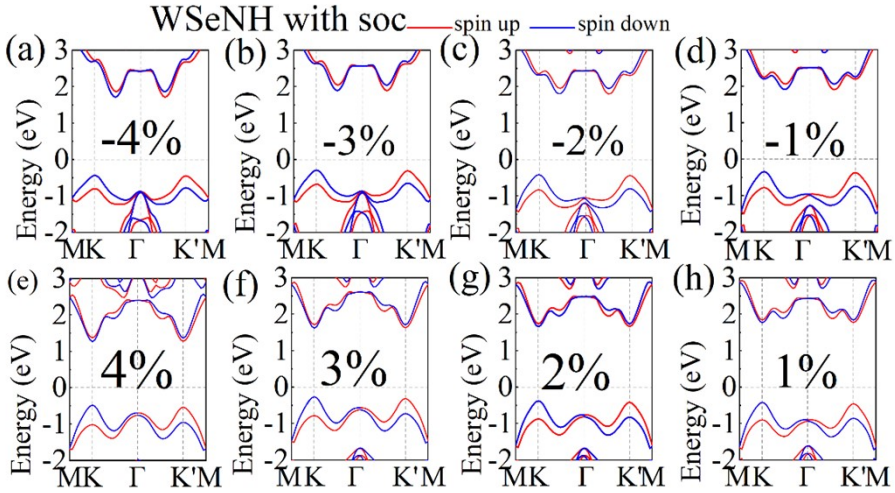
FigS12: (a-h) is a band plot at -4%-4% biaxial strain of CrSePH.



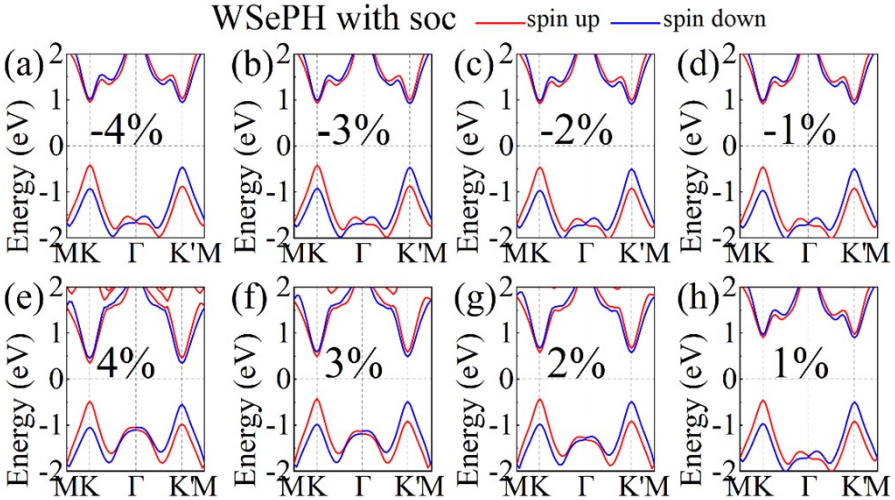
FigS13: (a-h) is a band plot at -4%-4% biaxial strain of MoSeNH.



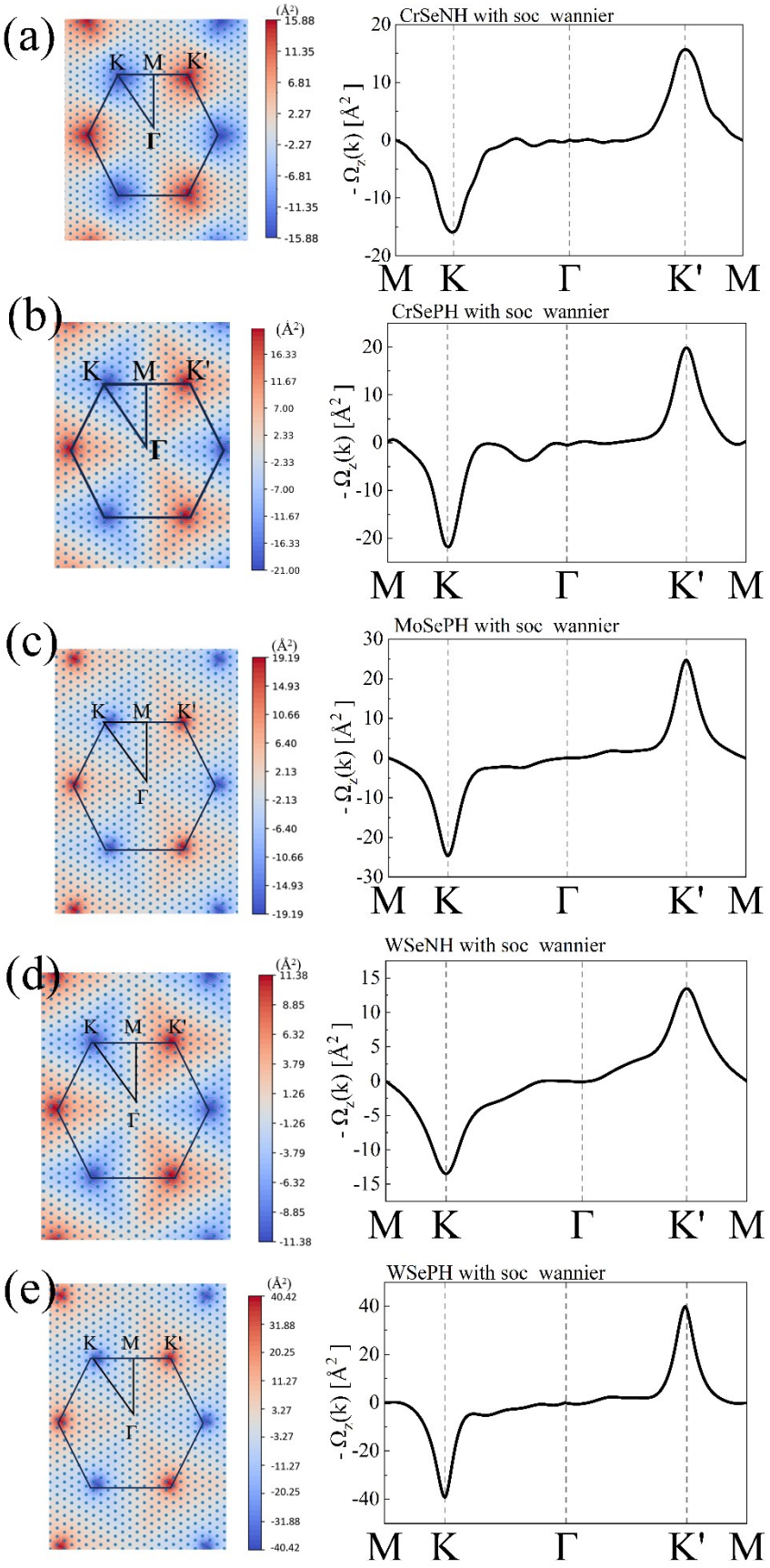
FigS14: (a-h) is a band plot at -4%-4% biaxial strain of MoSePH.



FigS15: (a-h) is a band plot at -4%-4% biaxial strain of WSeNH.



FigS16: (a-h) is a band plot at -4%-4% biaxial strain of WSePH.



Support **Fig.17**: (a-e) The left is Berry curvature of 1L MSeXH contour maps in the Brillouin zone and the right is along the high symmetry points.

Support **Table 1**: Bader Charges of 1L MSeXH (+: gain electrons; －: lose electrons)

	Matal	**Se**	**X（N / P）**	**H**
CrSeNH	－1.513	+0.377	+0.226	+0.910
CrSePH	－1.100	+0.633	－0.349	+0.817
MoSeNH	－1.368	+0.199	+0.602	+0.567
MoSePH	－0.596	+0.217	－0.459	+0.828
WSeNH	－1.396	+0. 213	+0.497	+0.686
WSePH	－1.254	+0.541	－0.110	+0.823

Support **Table 2**: the values of 1L MSeXH (M = Cr, Mo, W; X = N, P) monolayers' without soc E_g(enger band gap), *VSS* (valley spin splitting), with soc E_g(enger band gap), wannier berry is that Berry curvature calculated by Wann functionals, vasp berry is that Berry curvature calculated by Bloch.

	without soc E_g (eV)	*VSS (meV)*	*with soc* E_g*(eV)*	*wannier berry*（Å^2）	*vasp berry*（Å^2）
CrSeNH	1.296	99	1.070	16.02	15.88
CrSePH	1.151	185	1.025	21.30	21.00
MoSeNH	2.219	170	2.212	12.20	11.20
MoSePH	1.724	190	1.469	22.00	19.19
WSeNH	2.6	466	2.226	12.04	11.38
WSePH	1.556	495	1.246	42.00	40.42

The computational formalism for the spin-orbit in solid-state materials:

LSORBIT = .TRUE. (Activate SOC)

GGA-COMPAT = .FALSE. (Apply spherical cutoff on gradient field)

LMAXMIX = 4 (For d elements increase LMAXMIX to 4, f: LMAXMIX = 6)

1.LSORBIT = True switches on spin-orbit coupling (SOC) and automatically sets LNONCOLLINEAR = True. It requires using vasp-ncl. *SOC* couples the spin degrees of freedom with the lattice degrees of freedom.

2.GGA and METAGGA functionals might break the symmetry of the Bravais lattice slightly for cells that are not primitive cubic cells. The origin of this problem is subtle

and relates to the fact that the gradient field breaks the lattice symmetry for noncubic lattices. This can be fixed by setting GGA_COMPAT = .FALSE.

3.LMAXMIX controls up to which l-quantum number the one-center PAW charge densities are passed through the charge density mixer and written to the CHGCAR file.

Switching on SOC introduces an additional term to the Hamiltonian, given by: $H_{SOC}^{\alpha\alpha} \propto \sigma * L$

where σ is the Pauli spin operator and L is the angular momentum operator. This term couples the spin and orbital degrees of freedom. As a relativistic correction, *SOC* is most significant near the nuclei, and it is assumed that contributions of H_{SOC} outside the *PAW* (Projector Augmented Wave) spheres are negligible. Therefore, VASP (Vienna Ab initio Simulation Package) only calculates the matrix elements of H_{SOC} for the all-electron one-center contributions:

$$E_{soc}^{ij} = \sigma_{RiRj}\sigma_{lilj}\sum_{nk} w_k f_{nk} \sum_{\alpha\beta} \left\langle \psi_{nk}^{\sim\alpha} \middle| p_i^{\sim} \right\rangle \left\langle \Phi_i \middle| H_{SOC}^{\alpha\beta} \middle| \Phi_j \right\rangle \left\langle p_j^{\sim} \middle| \psi_{nk}^{\sim\beta} \right\rangle$$

Where $\Phi_i(r) = R_i(|r - R_i|)Y_{limi}(\theta, \varphi)$ are the partial waves of an atom centered at R_i, $\psi_{nk}^{\sim\alpha}$ is the spinor-componentα=↑, ↓ of the pseudo-orbital with band-index n and Bloch vector k, and f_{nk} and ω_k are the Fermi- and k-point weights, respectively. t is possible to write the partial magnetization by setting LORBIT, i.e., the site- and orbital-resolved expectation value of the Pauli-spin operator σ. And the partial orbital angular momentum by setting LORBMOM, i.e., the site- and orbital-resolved expectation value of the orbital angular momentum operator *L*.

POSCAR files:

```
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     2.9975392168889126       0.0000000000000000       0.0000000000000000
    -1.4752028917514424       2.5552453737443490       0.0000000000000000
     0.0000000000000000       0.0000000000000000      22.6000003814999992
   N      Se     Cr     H
     1      1      1      1
Direct
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  0.9831387997087049  0.0169453618532316  0.4516641557712973
  0.6498053994389039  0.3502779731019672  0.5261371309896106
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0.0000000000000000 0.0000000000000000 22.6000003814999992
P Se Cr H
1 1 1 1
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MoSeNH
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MoSePH\(0\0\1)\(2)
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WSeNH
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WSePH
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