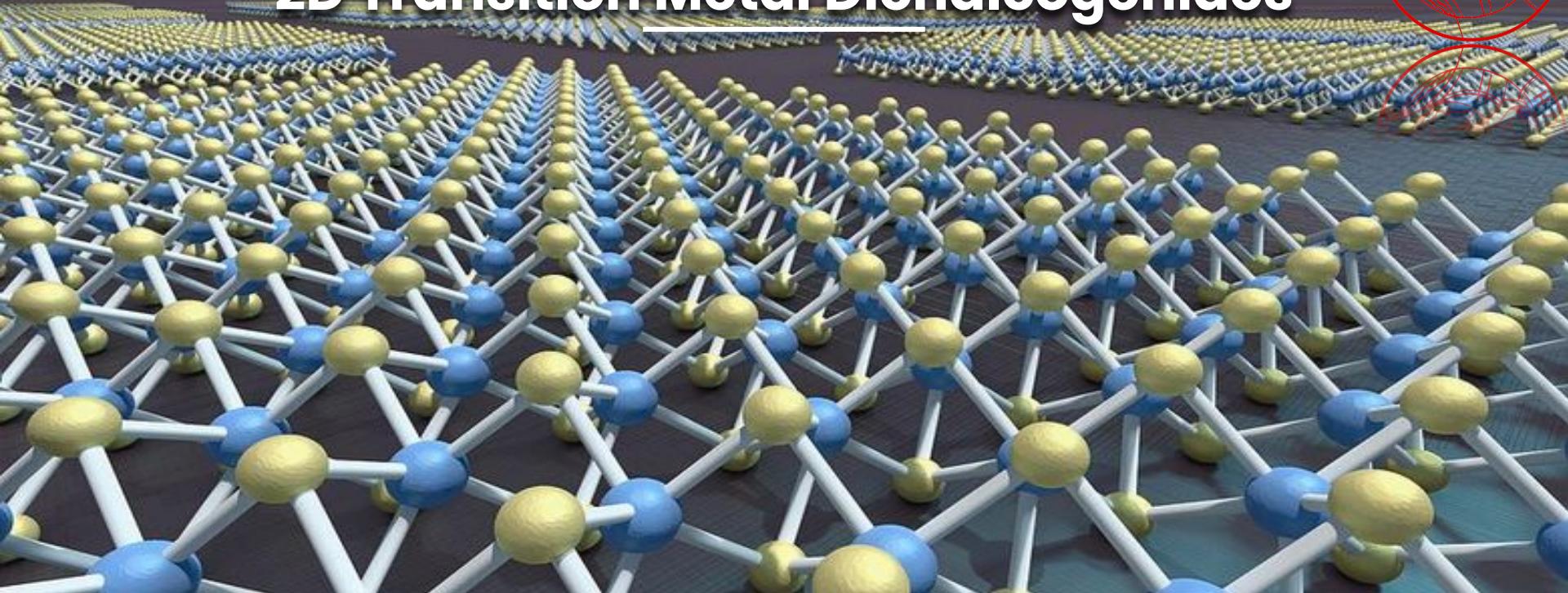


# Band Structure and Density of States of 2D Transition Metal Dichalcogenides



**Professors:** Kopidakis Georgios, Remediakis Ioannis

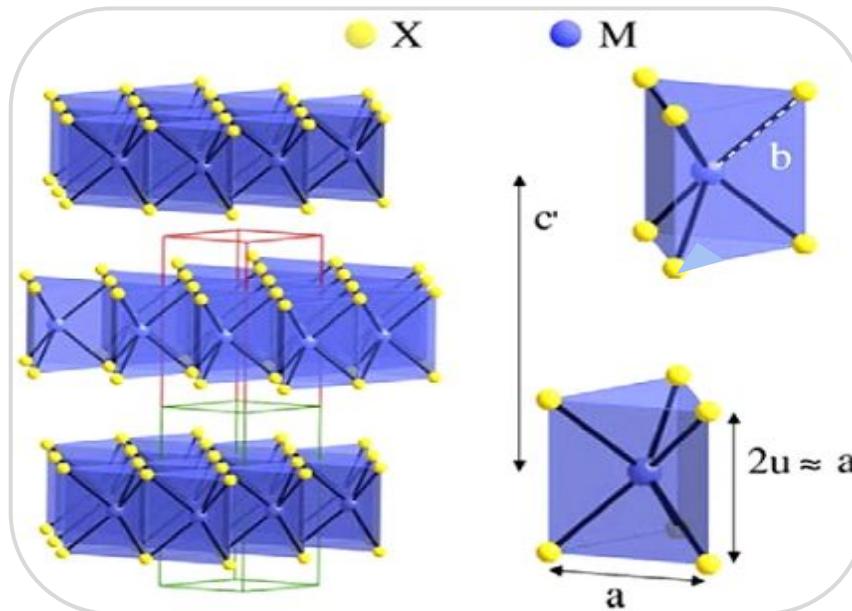
**Student:** Vourvachakis Georgios

**Date:** 21/05/2025

Image description: Artistic representation of a TMD monolayer [[sciencephotogallery.com](http://sciencephotogallery.com)]

# Semiconducting Group-VI TMDs: $\text{MX}_2$ ( $\text{M} \in \{\text{Mo, W}\}$ and $\text{X} \in \{\text{S, Se, Te}\}$ )

**Unit Layer:** Hexagonal layer of M atoms sandwiched between atomic layers of X atoms



# Semiconducting Group-VI TMDs: $\text{MX}_2$ (M ∈ {Mo, W} and X ∈ {S, Se, Te})

**Unit Layer:** Hexagonal layer of M atoms sandwiched between atomic layers of X atoms

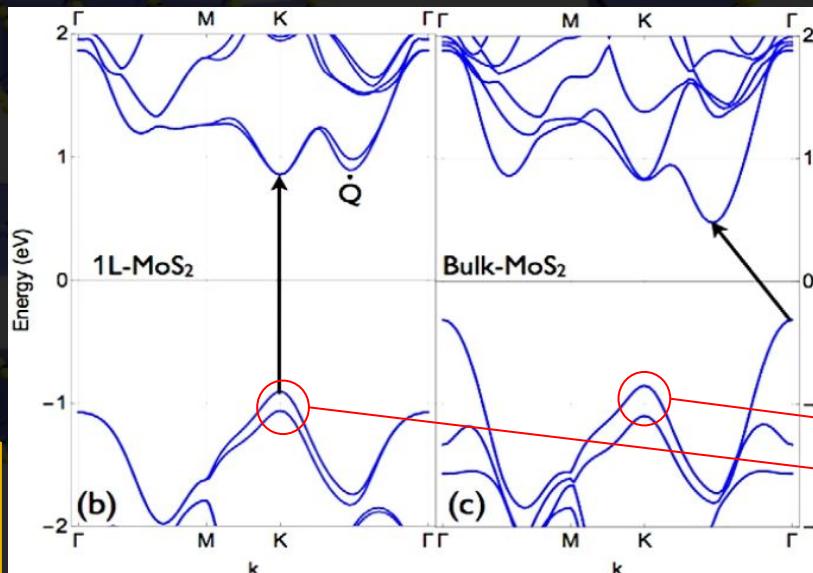
( $xy$ ,  $x^2-y^2$ , and  $3z^2-r^2$  d-orbitals of M) ⊕ (p-orbitals of X) → HOMO / LUMO

	Monolayer	Bilayer	Bulk
$\text{MoS}_2$	1.715	1.710–1.198	1.679–0.788
$\text{WS}_2$	1.659	1.658–1.338	1.636–0.917
$\text{MoSe}_2$	1.413	1.424–1.194	1.393–0.852
$\text{WSe}_2$	1.444	1.442–1.299	1.407–0.910
$\text{ReSe}_2$	1.43	—	1.35

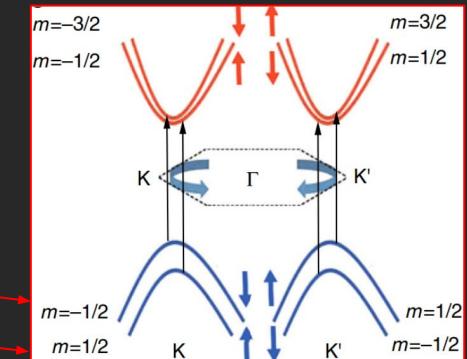
↓ dielectric screening effect



↑ optical  $E_g$

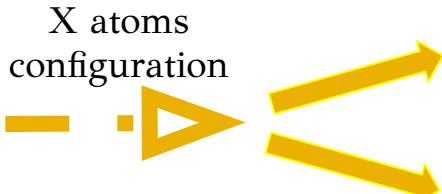


SOC-induced band splitting



# Polymorphism in 2D Group-VI TMDs

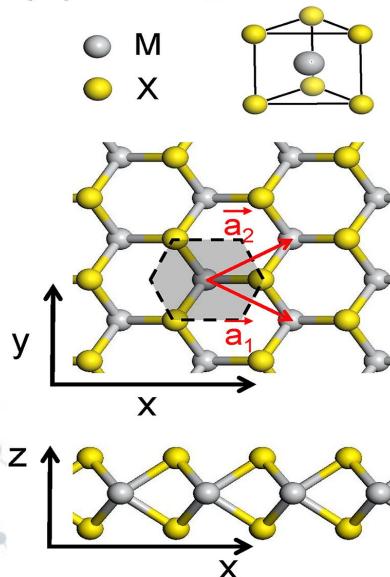
Polymorphism



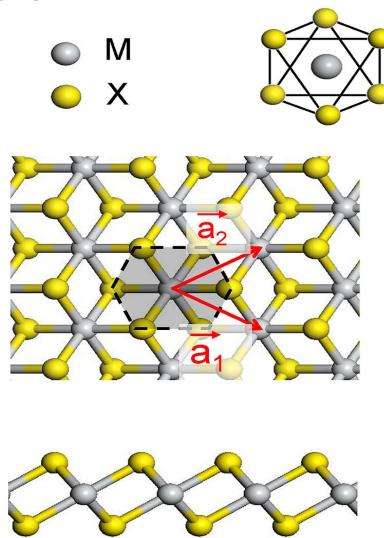
Trigonal Prismatic H ( $D_{3h}$ )

Octahedral T ( $O_h$ )

(a)  $H\text{-MX}_2$  (Trigonal)

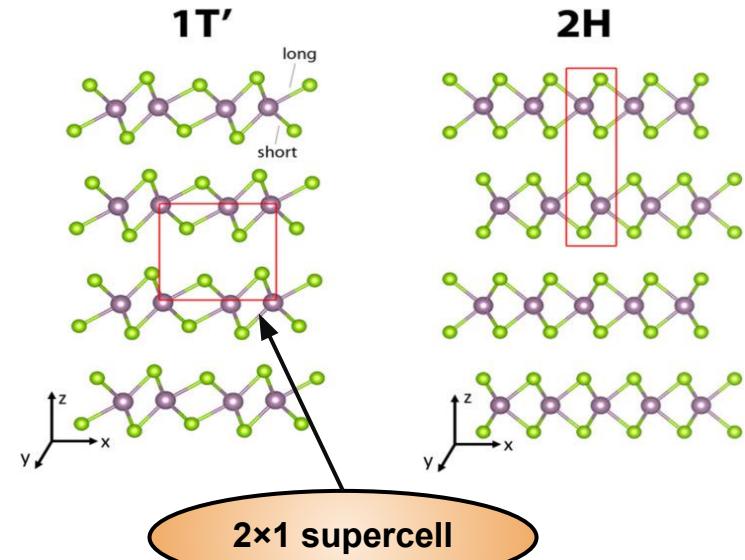
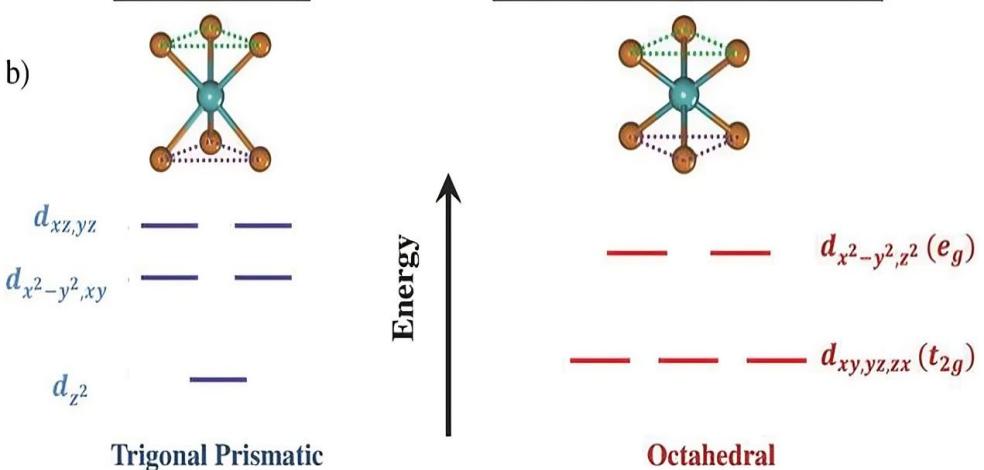
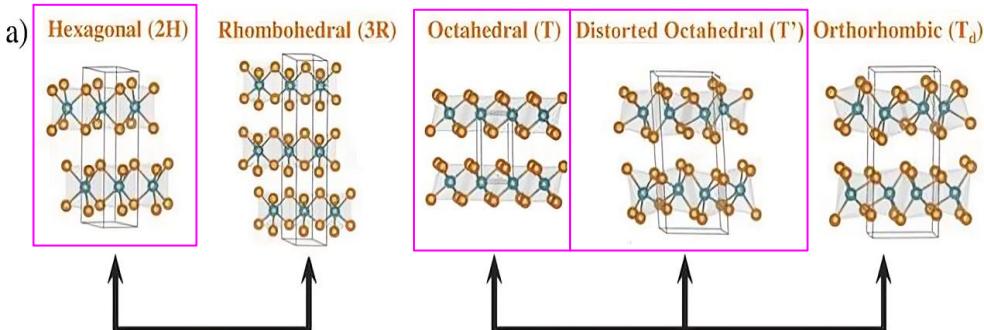


(b)  $T\text{-MX}_2$  (Octahedral)



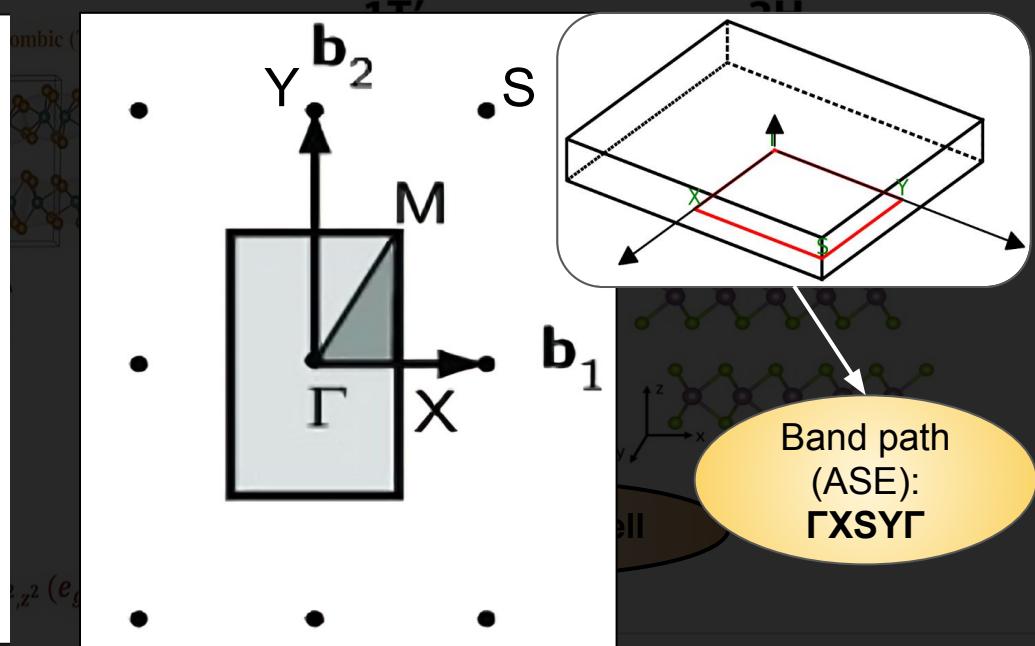
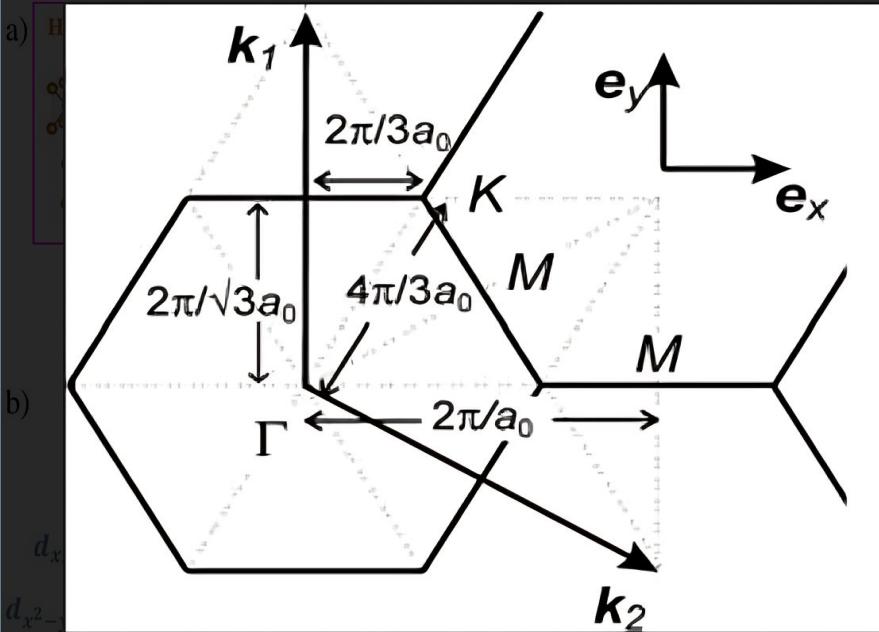
- Hexagonal lattices
- **Basis:** one atom M in the middle and two chalcogen atoms X on the edges.
- “ABA” and “ABC” atomic stacking sequences (X-M-X).

# Polymorphism in 2D Group-VI TMDs



- A. Bonding and stacking modes.
- B. Comparison of d-orbital splitting (*no SOC*) in 1H and 1T phases, respectively.

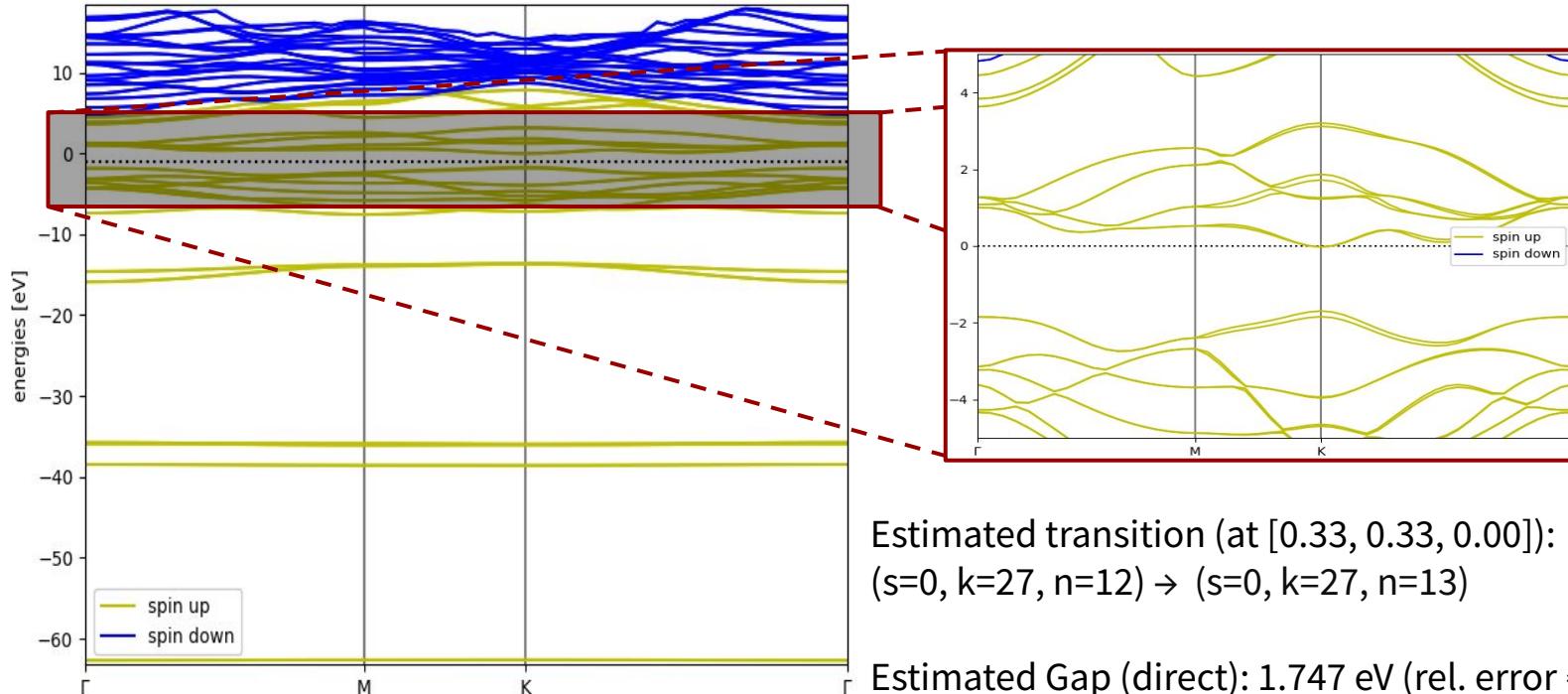
# Polymorphism in 2D Group-VI TMDs



Band path  
(ASE):  
 $\Gamma \text{MK}\Gamma$

The  $1T'$  supercell lowers the in-plane symmetry to **orthorhombic** (space group:  $Pnm2_1$ ,  $\mathbf{a}_1 \neq \mathbf{a}_2$ )  $\rightarrow$  **rectangular BZ**.

# Results on Sulfides: MoS<sub>2</sub> (1H)



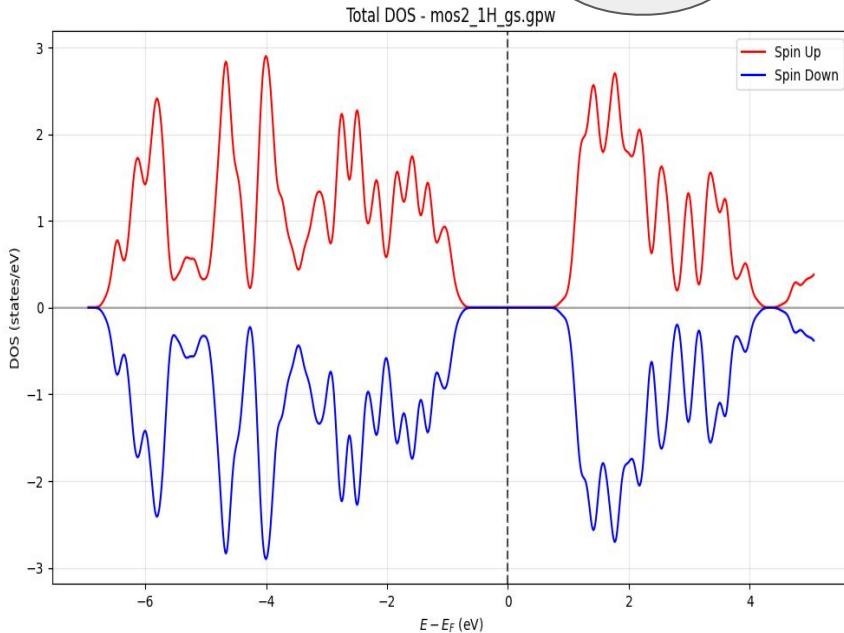
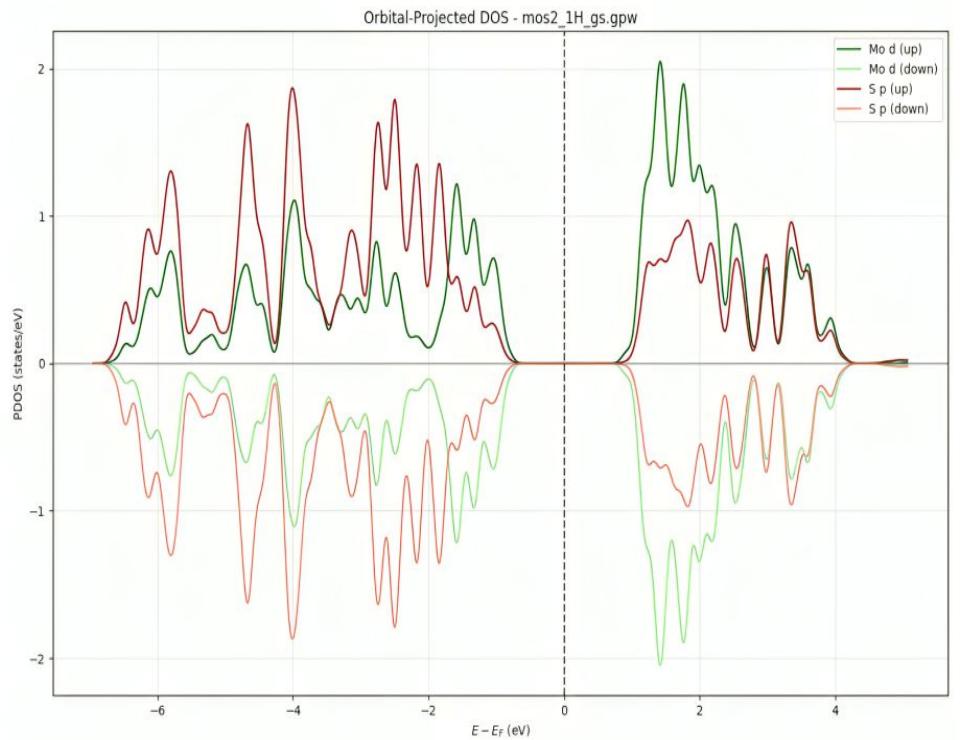
Estimated transition (at [0.33, 0.33, 0.00]):  
(s=0, k=27, n=12)  $\rightarrow$  (s=0, k=27, n=13)

Estimated Gap (direct): 1.747 eV (rel. error  $\approx$  8.05%)  
PL adsorption E<sub>g</sub> (\*): 1.90 eV

Hyperparameters:  $a_{\text{MoS}_2} = 3.16 \text{ \AA}$ (\*), PW cutoff: 400 eV, k-points:  $12 \times 12 \times 1$ , vacuum: 20.0 eV, spinpol=True, xc: GGA-PBE, FD smearing ( $\sigma$ ): 0.01 eV, mixer: Pulay (default)    (\*)[Splendiani et al., Nano Letters **10**(4), 1271-5 (2010)]

# Results on Sulfides: MoS<sub>2</sub> (1H)

The (total) DOS is a measure of the **number of electronic states per unit energy per unit volume**.



Integrated electron count up to  $E_F$ :

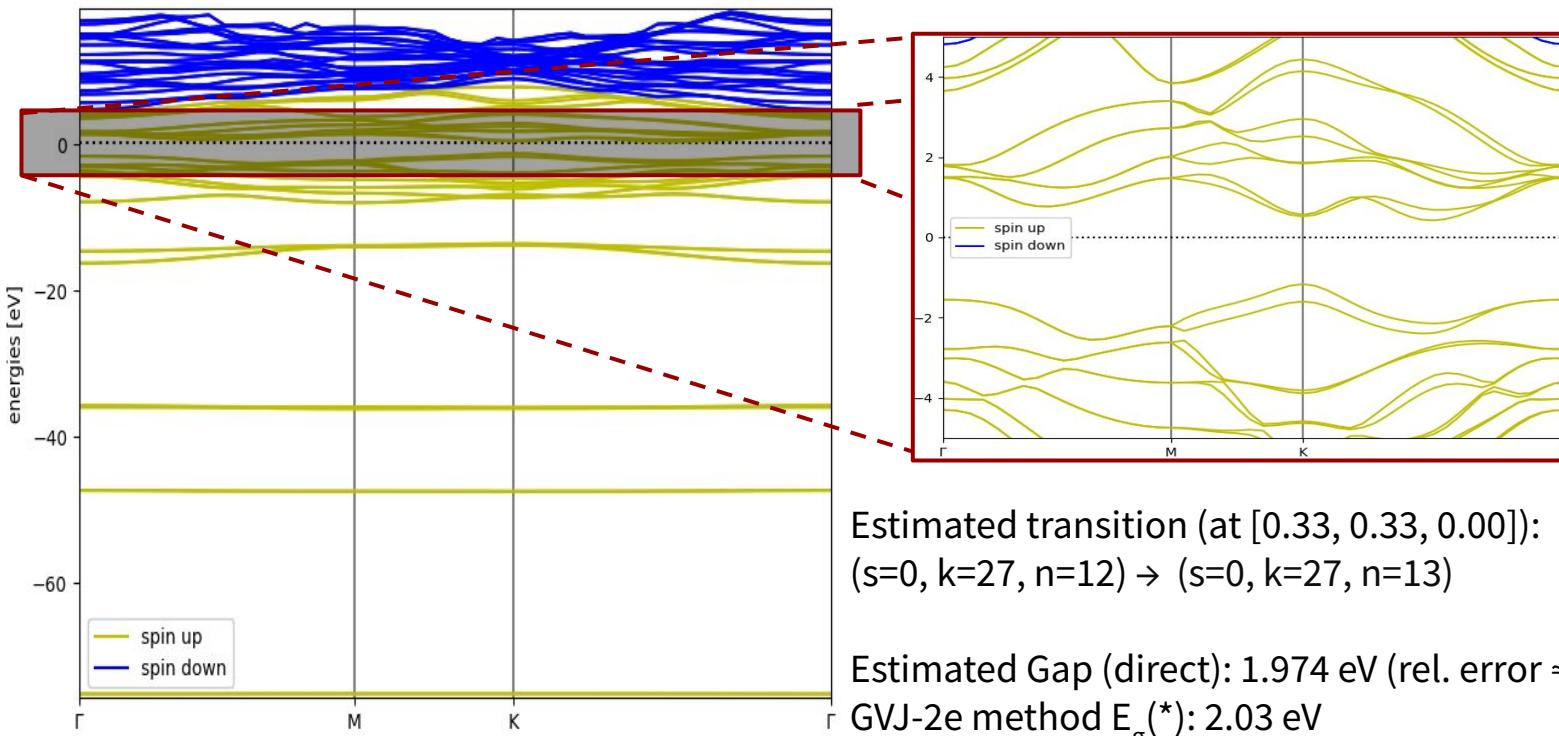
Spin up: 6.948 e<sup>-</sup>

Spin down: 6.948 e<sup>-</sup>

Zero net spin polarization

**Orbital-projected density of states (PDOS)** projects DOS onto specific atomic orbitals or molecular states.

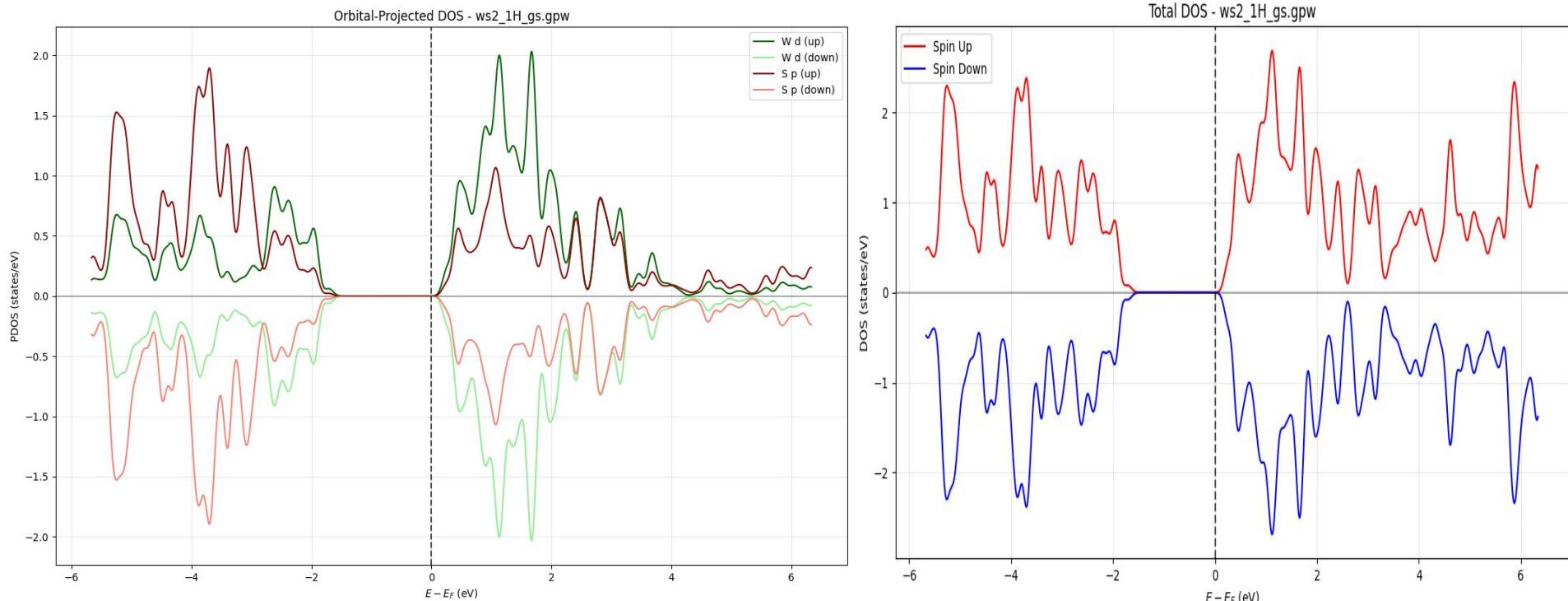
# Results on Sulfides: $\text{WS}_2$ (1H)



Hyperparameters:  $a_{\text{WS}_2} = 3.15 \text{ \AA}$ (\*), PW cutoff: 400 eV, k-points:  $12 \times 12 \times 1$ , vacuum: 20.0 eV, spinpol=True, xc: GGA-PBE,  $\sigma$ : 0.01 eV, mixer: Pulay (default)

(\*)[Julia Gusakova et al., Phys. Status Solidi A, 214: 1700218 (2017)]

# Results on Sulfides: $\text{WS}_2$ (1H)



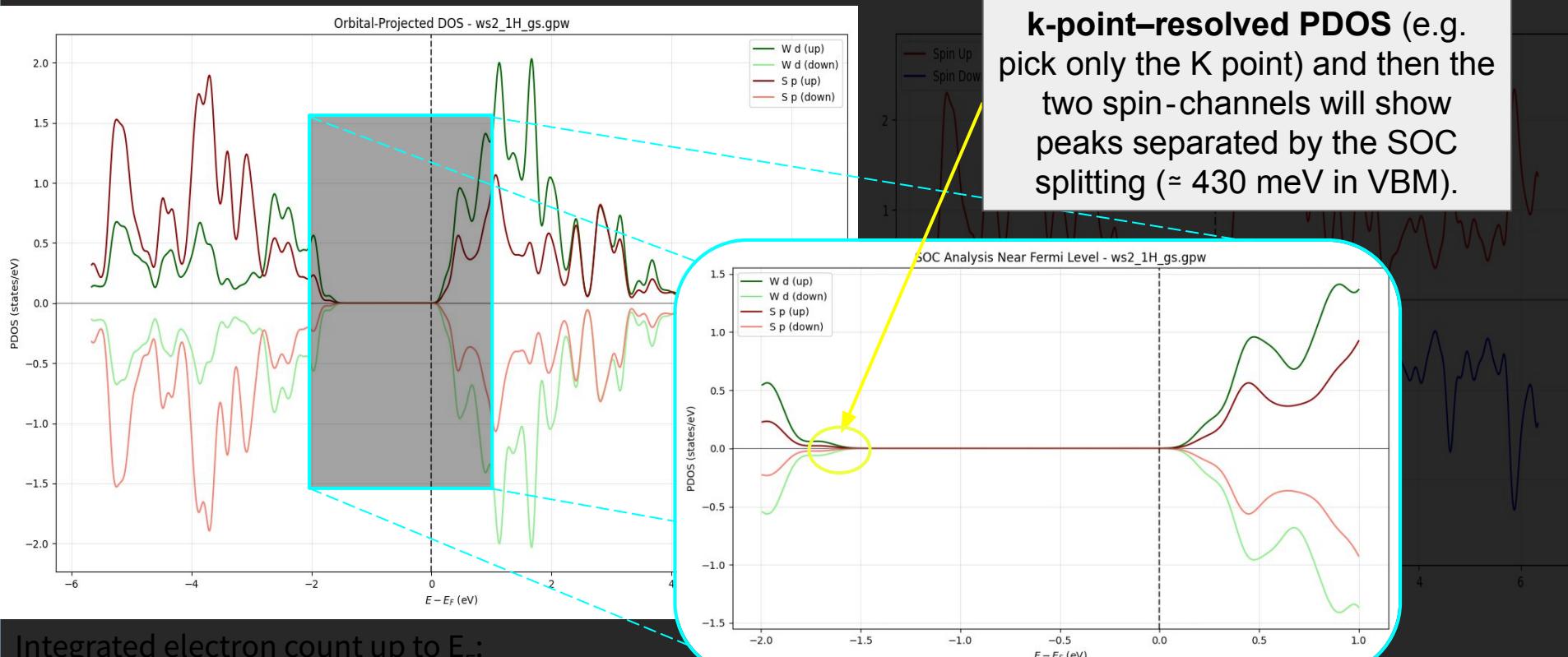
Integrated electron count up to  $E_F$ :

Spin up: 4.457 e<sup>-</sup>

Spin down: 4.457 e<sup>-</sup>

Zero net spin polarization

# Results on Sulfides: $\text{WS}_2$ (1H)



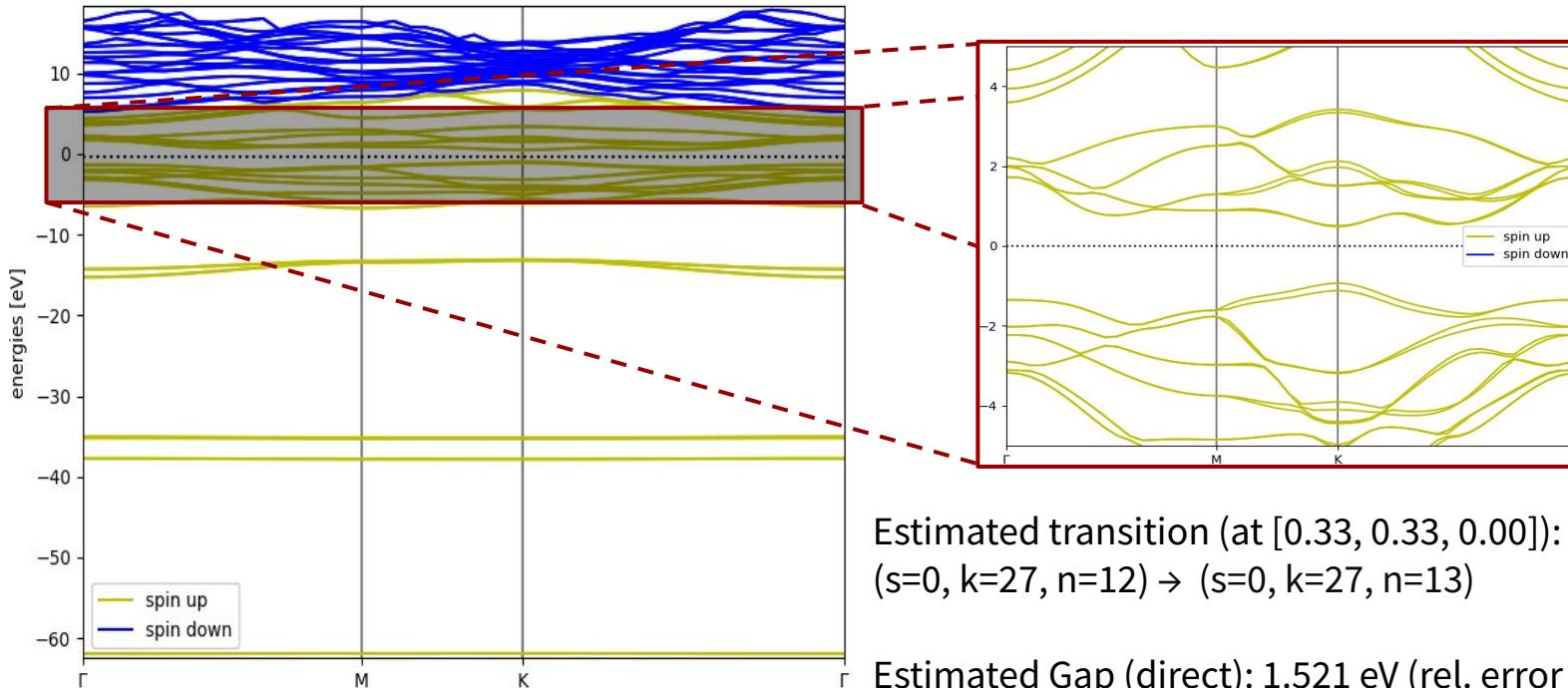
Integrated electron count up to  $E_F$ :

Spin up: 4.457  $e^-$

Spin down: 4.457  $e^-$

Zero net spin polarization

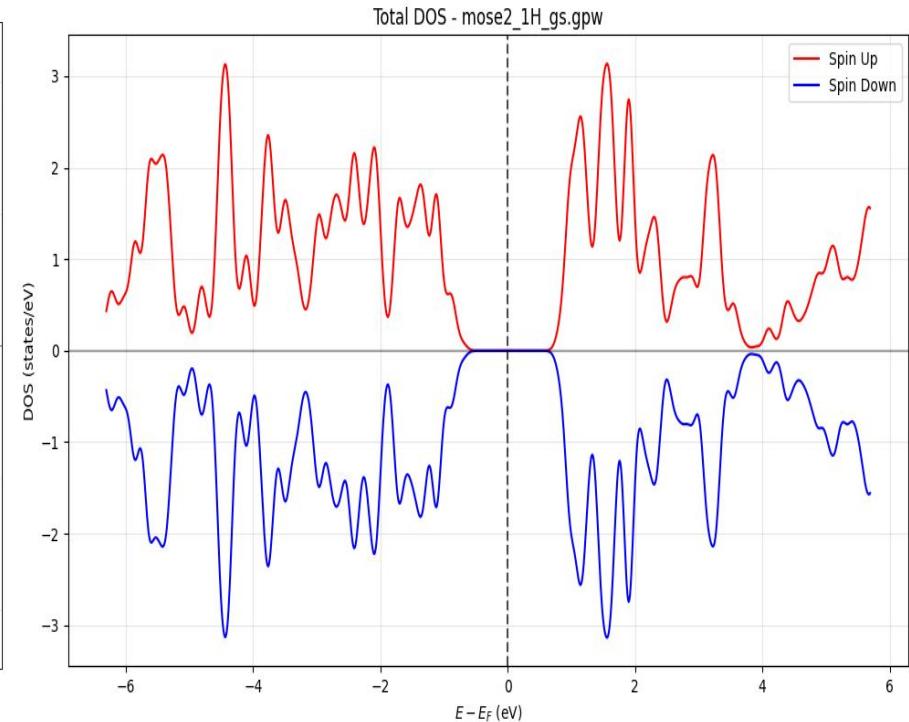
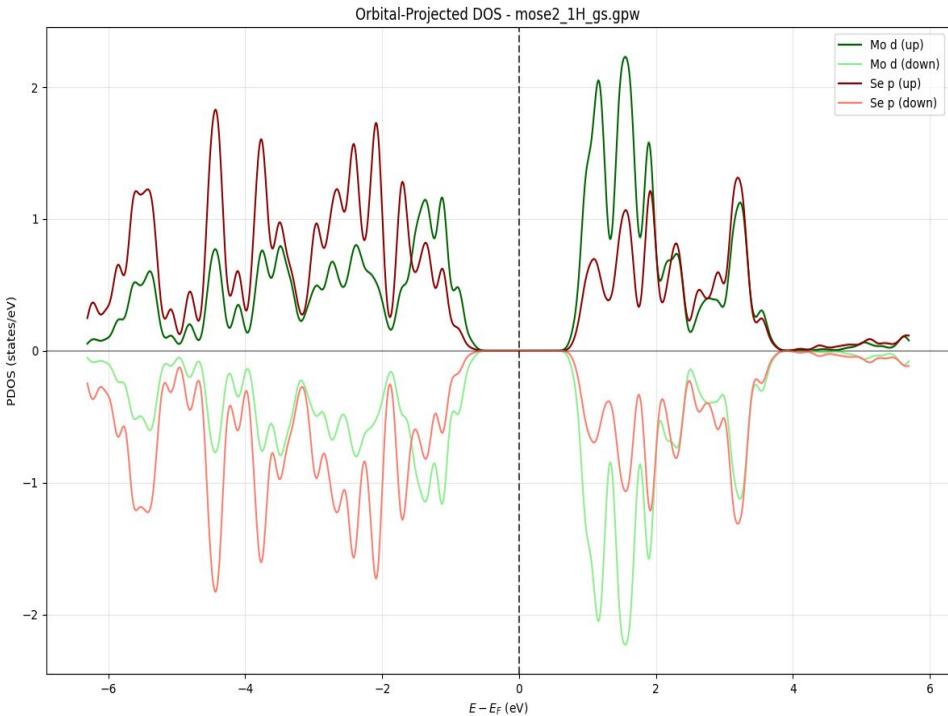
# Results on Selenides: MoSe<sub>2</sub> (1H)



Hyperparameters:  $a_{\text{MoSe}_2} = 3.29$  Å<sup>(\*)</sup>, PW cutoff: 400 eV, k-points: 12×12×1, vacuum: 20.0 eV, spinpol=True, xc: GGA-PBE, σ: 0.01 eV, mixer: Pulay (default)

(\*)[T. Godde et al., Phys. Rev. B, **94**, 165301 (2016)]

# Results on Selenides: MoSe<sub>2</sub> (1H)



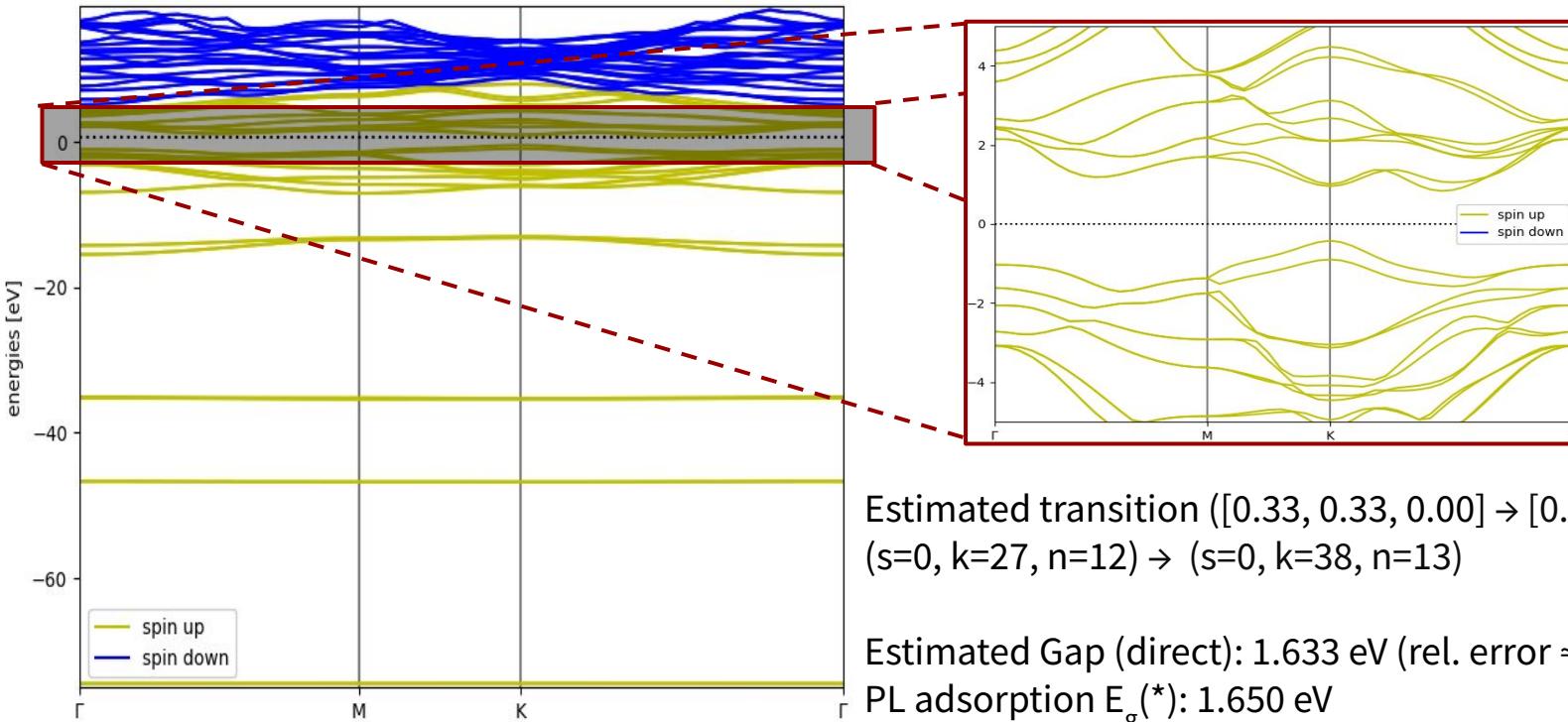
Integrated electron count up to  $E_F$ :

Spin up: 6.962 e<sup>-</sup>

Spin down: 6.962 e<sup>-</sup>

Zero net spin polarization

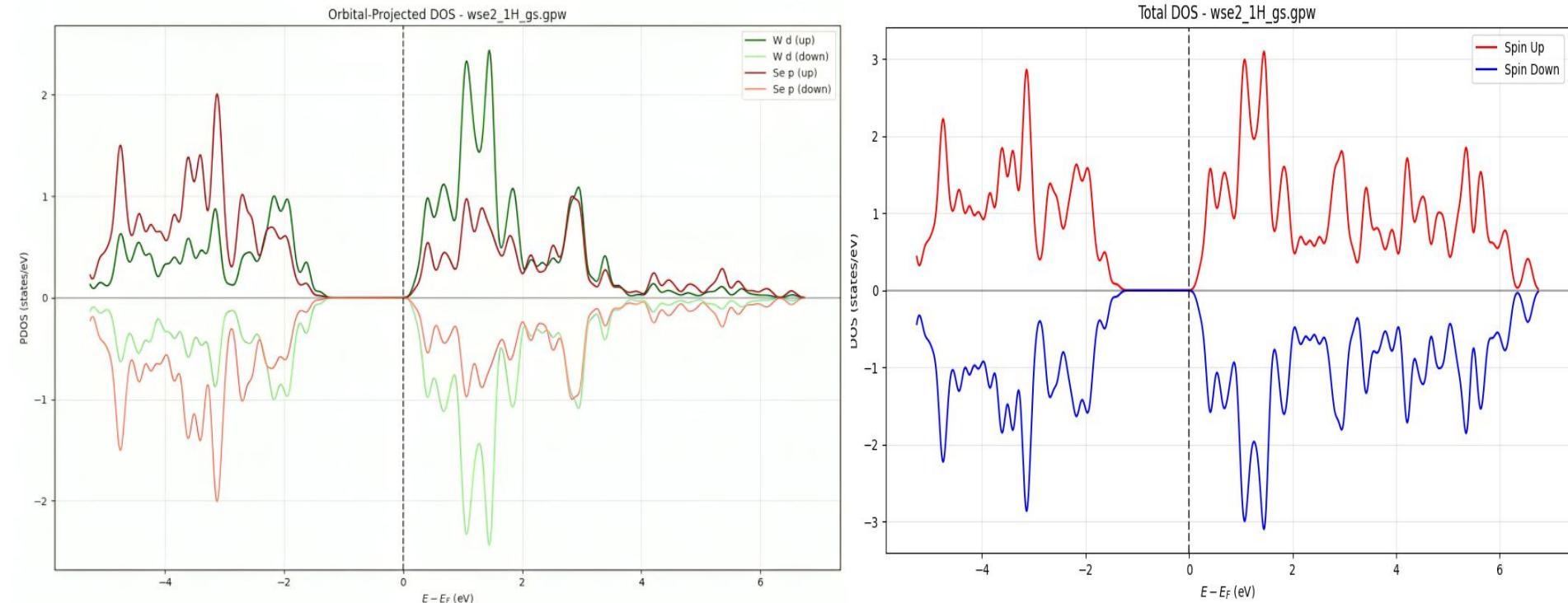
# Results on Selenides: WSe<sub>2</sub> (1H)



Hyperparameters:  $a_{\text{WSe}_2} = 3.28 \text{ \AA}$ (\*), PW cutoff: 400 eV, k-points: 12×12×1, vacuum: 20.0 eV, spinpol=True, xc: GGA-PBE,  $\sigma$ : 0.01 eV, mixer: Pulay (default)

(\*)[T. Godde et al., Phys. Rev. B, **94**, 165301 (2016)]

# Results on Selenides: WSe<sub>2</sub> (1H)



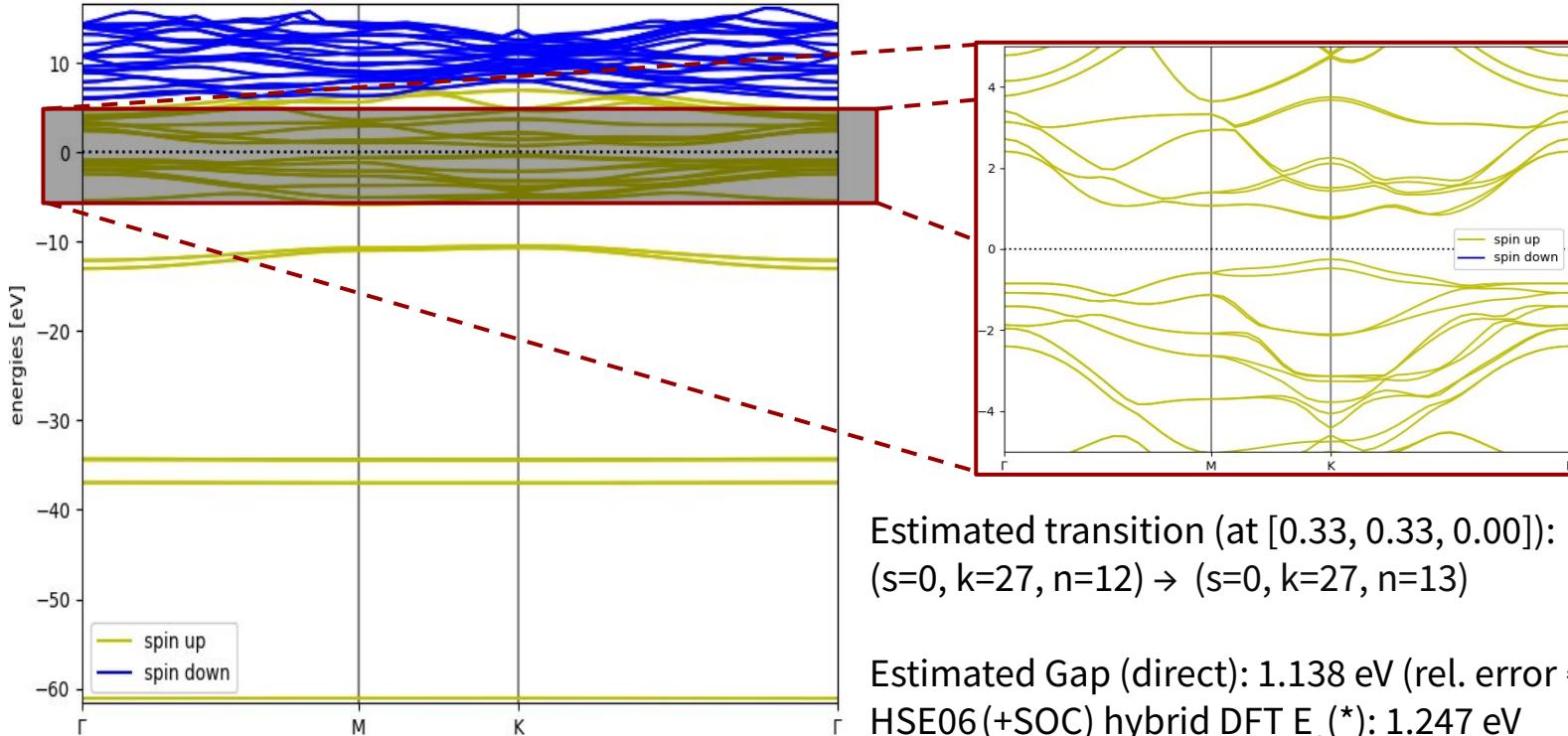
Integrated electron count up to  $E_F$ :

Spin up: 5.085 e<sup>-</sup>

Spin down: 5.085 e<sup>-</sup>

Zero net spin polarization

# Results on Tellurides: MoTe<sub>2</sub> (1H)

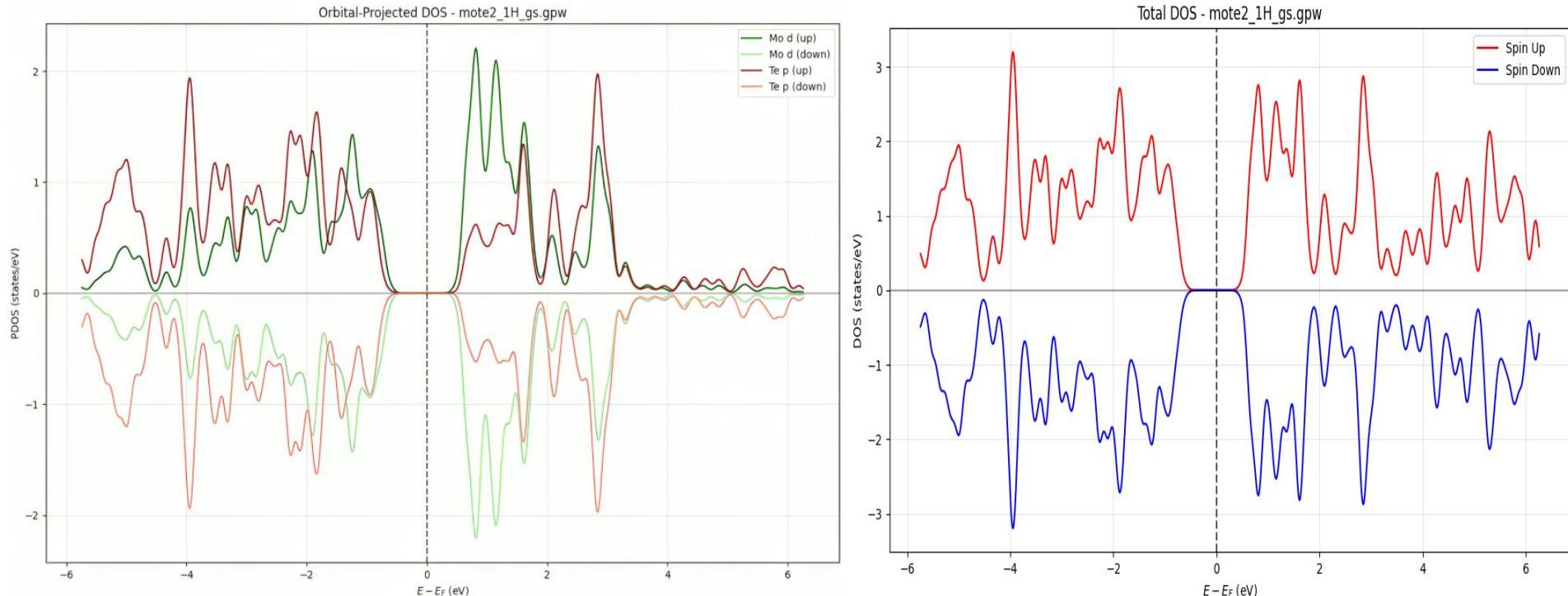


Hyperparameters:  $a_{\text{MoTe}_2} = 3.52 \text{ Å}$ (\*), PW cutoff: 400 eV, k-points:  $12 \times 12 \times 1$ , vacuum: 20.0 eV, spinpol=True, xc: GGA-PBE,  $\sigma$ : 0.01 eV, mixer: Pulay (default)

(\*)[Chu Qing et al., PCCP, accepted in April 22 (2025)]

CBM: 0.504 eV  
VBM: -0.635 eV  
 $\Delta^V_{\text{so}} \approx 219 \text{ meV}$

# Results on Tellurides: MoTe<sub>2</sub> (1H)



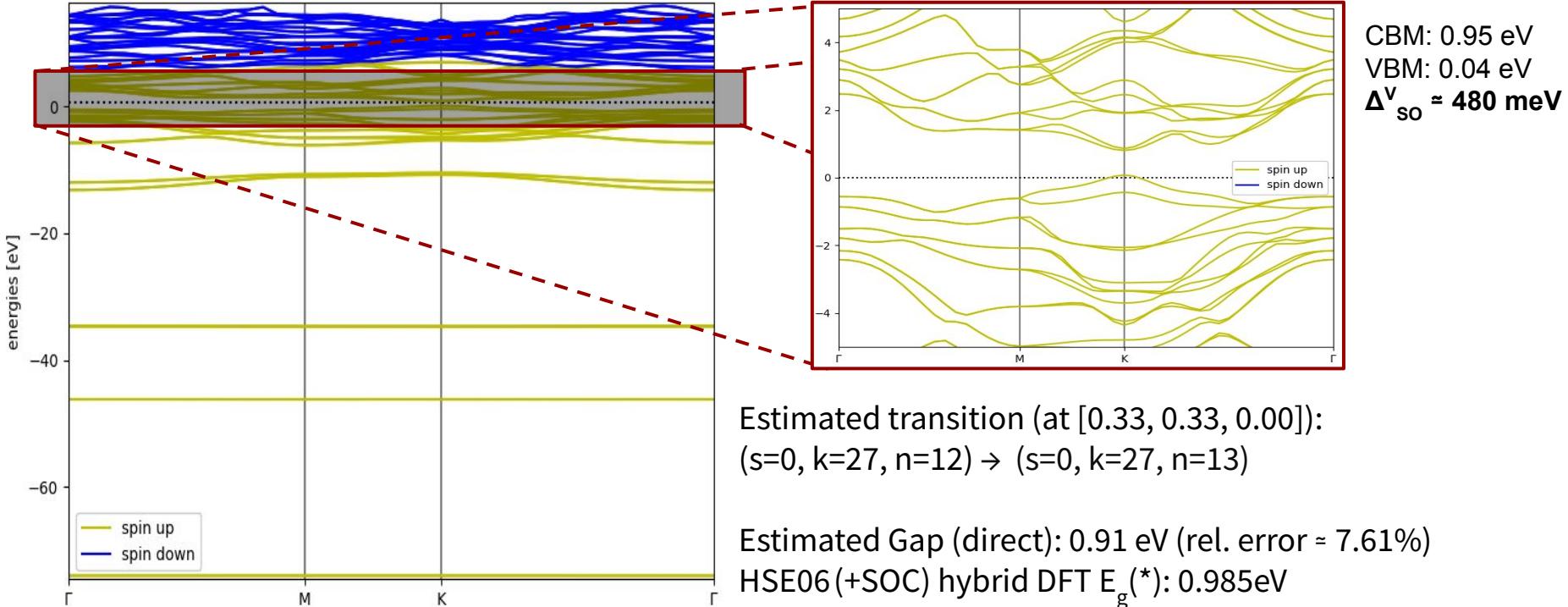
Integrated electron count up to  $E_F$ :

Spin up: 6.847 e<sup>-</sup>

Spin down: 6.847 e<sup>-</sup>

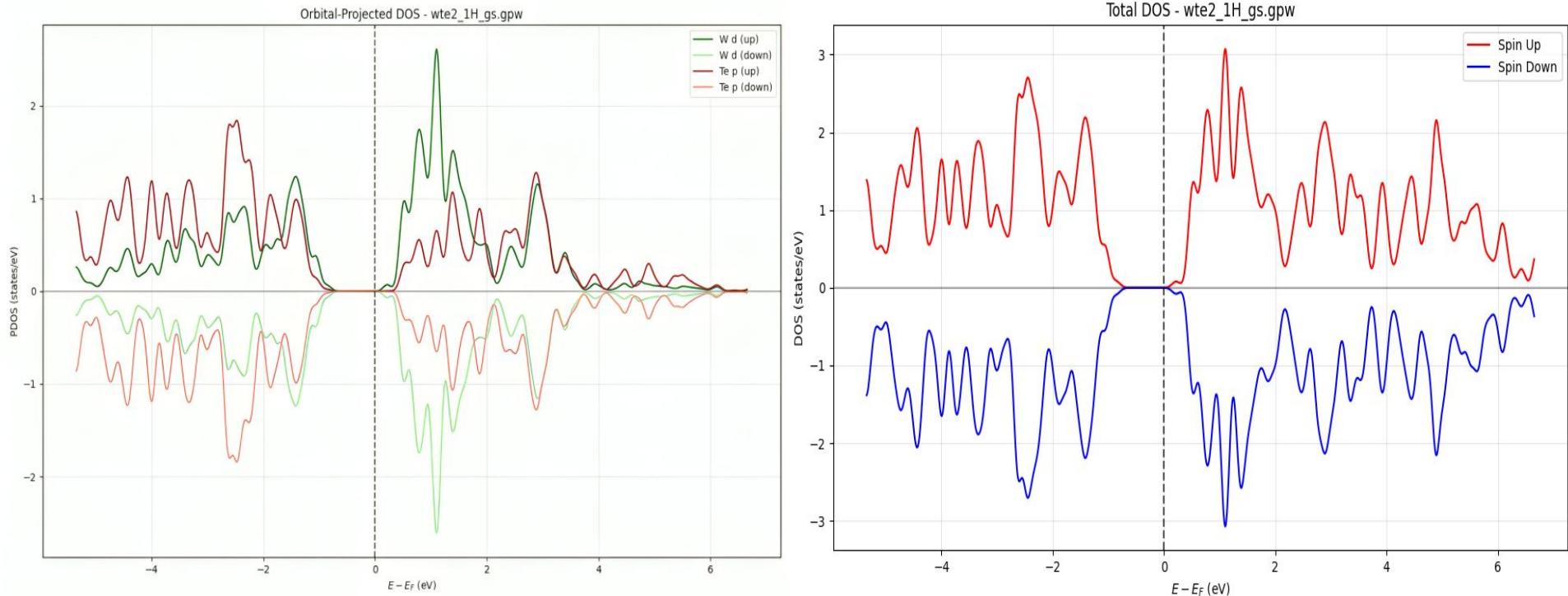
Zero net spin polarization

# Results on Tellurides: WTe<sub>2</sub> (1H)



(\*)[H. H. Huang et al., PCCP, 18, 4086-4094 (2016)]

# Results on Tellurides: WTe<sub>2</sub> (1H)



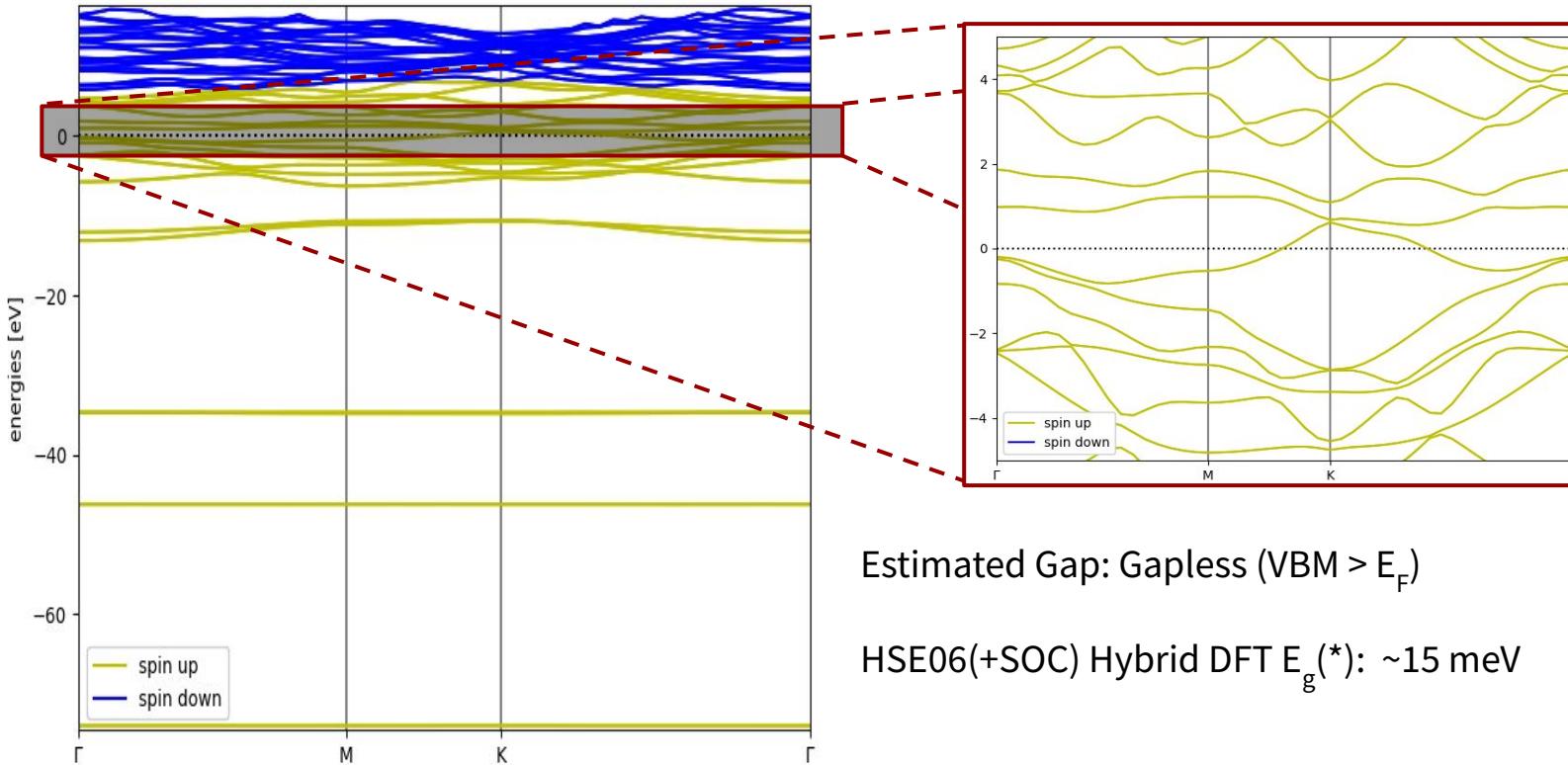
Integrated electron count up to  $E_F$ :

Spin up: 6.066 e<sup>-</sup>

Spin down: 6.066 e<sup>-</sup>

Zero net spin polarization

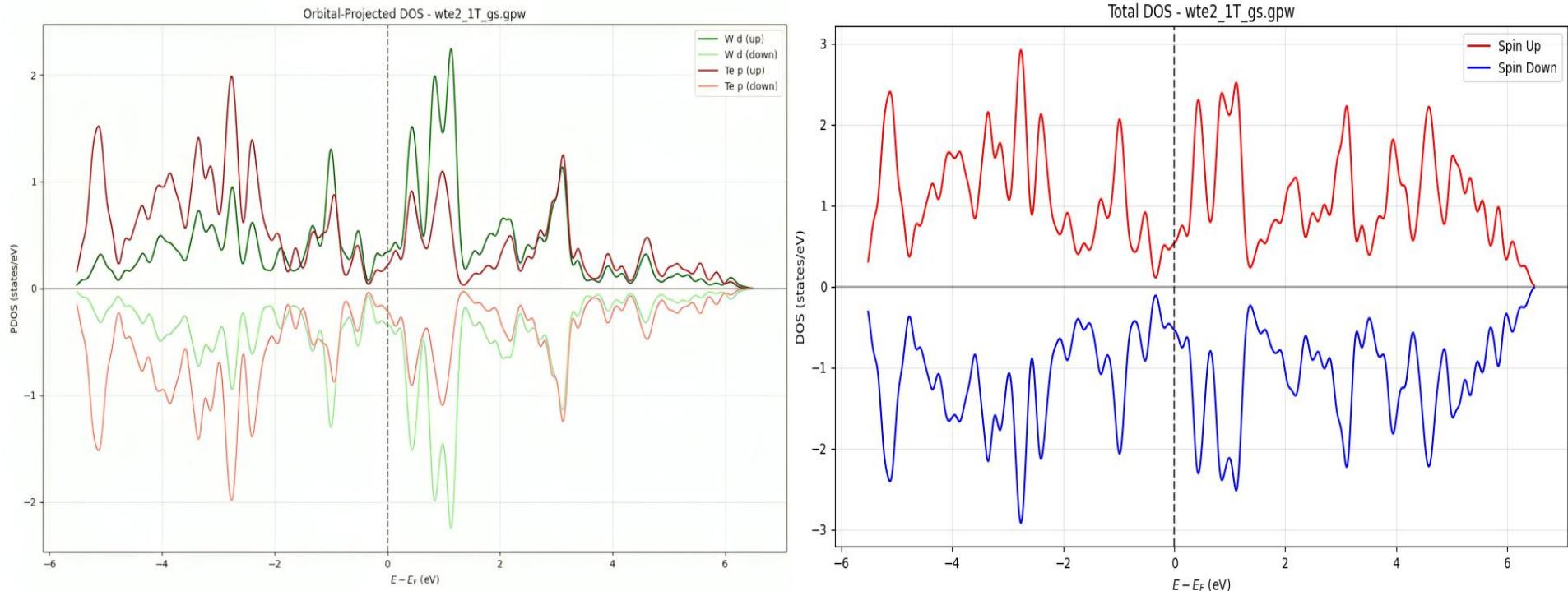
# Results on Tellurides: WTe<sub>2</sub> (1T)



Hyperparameters: a<sub>WTe<sub>2</sub></sub>=3.56 Å(\*), PW cutoff: 400 eV, k-points: 12×12×1, vacuum: 20.0 eV, spinpol=True, xc: GGA-PBE, σ: 0.01 eV, mixer: Pulay (default)

(\*)[Feipeng Zheng et al., Adv. Mat. **28**(24) (2016)]

# Results on Tellurides: WTe<sub>2</sub> (1T)



Integrated electron count up to  $E_F$ :

Spin up: 6.909 e<sup>-</sup>

Spin down: 6.909 e<sup>-</sup>

Zero net spin polarization

# Case study on 1T'-WTe<sub>2</sub>: DFT+U, multi-step approach

Non-magnetic (*spinpol = False*), non-Hubbard workflow (unrelaxed)

## 1. Coarse SCF (preconditioning):

k-points: 5×5×1, σ: 0.01eV, maxiter: 100 (conv: 73)

Pulay(nmaxold=5→3, weight=50.0→100.0) (aggressive, fast convergence)

## 2. Intermediate spin-polarized:

k-points: 10×10×1, σ: 0.02 eV, maxiter: 50 (conv: 28)

Pulay(nmaxold=5→3, β=0.05→0.03) (softer, moderate convergence)

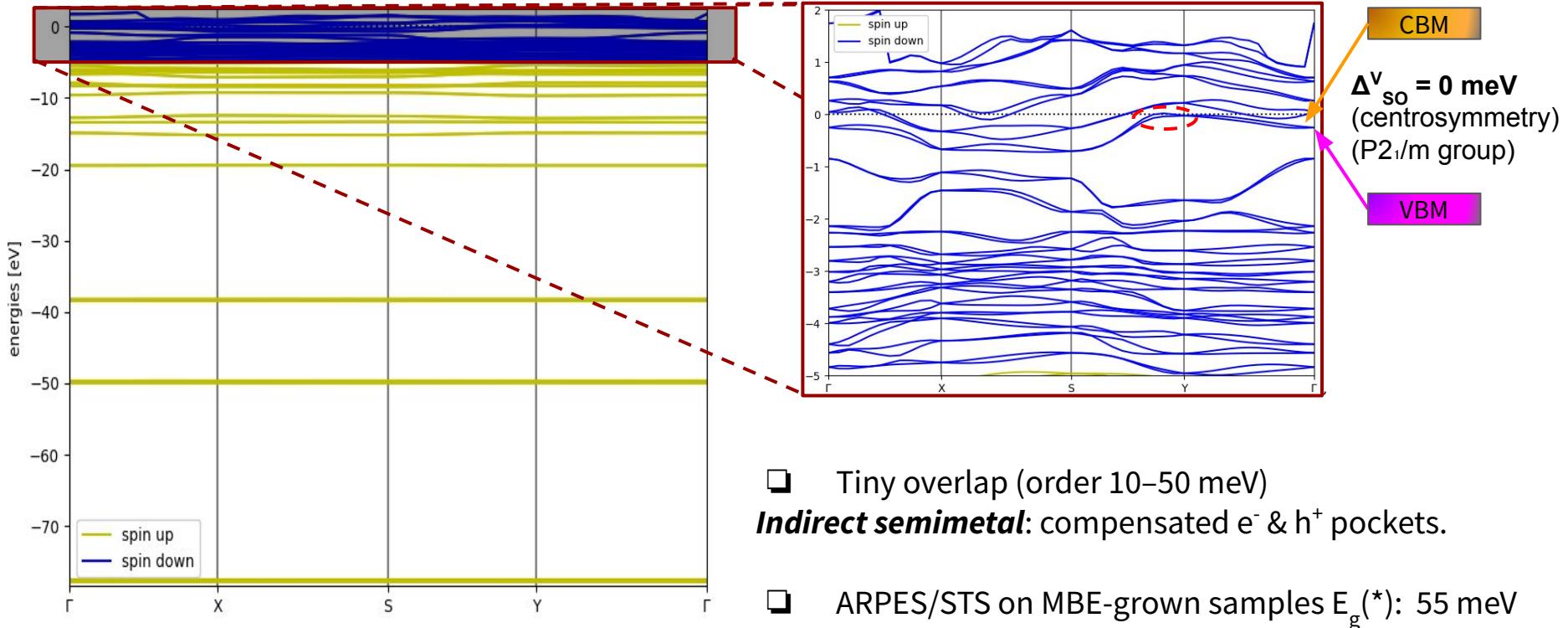
## 3. Full target k-point sampling SCF:

k-points: 15×15×1, σ: 0.02 eV, maxiter: 50 (conv: 27)

Pulay(nmaxold=5→8, β=0.05→0.04) (more history, improved accuracy)

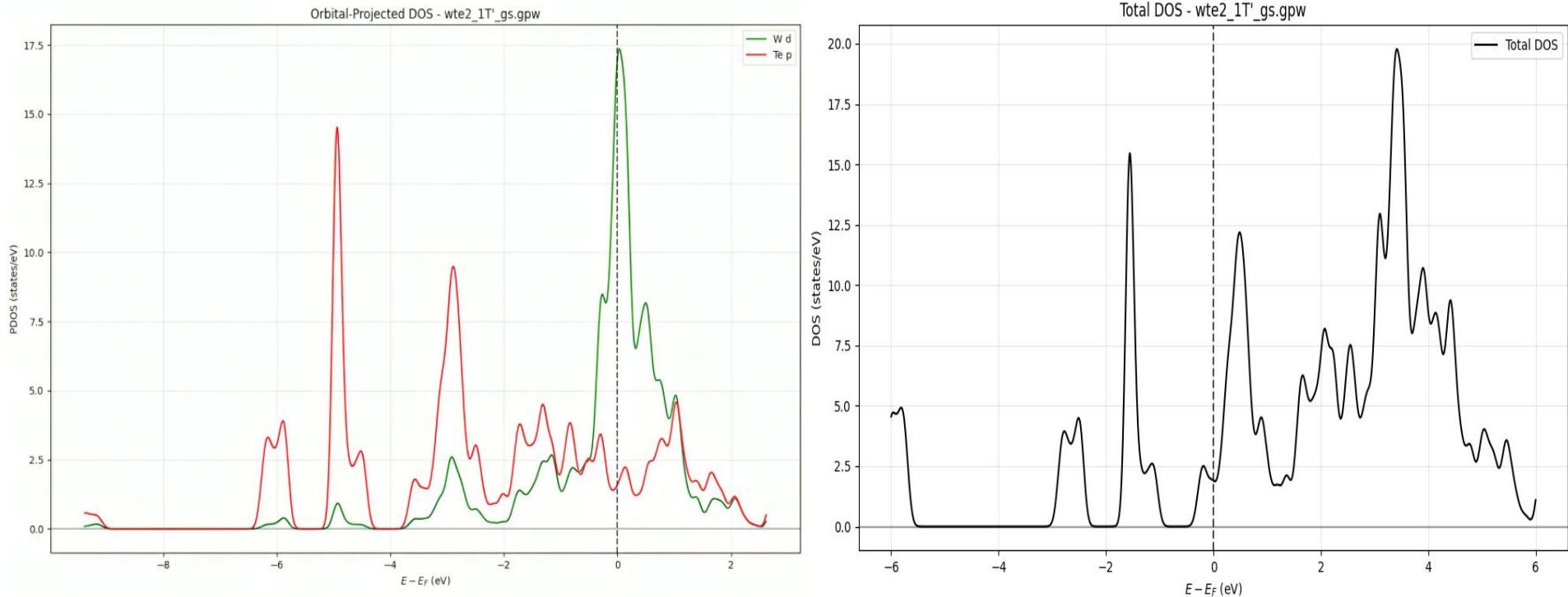
*Hubbard U parameter (W-based): 2.5-2.8 eV(\*\*) (fails to converge (> 16 hours)  
with spinpol=True and magmoms ...) [see './fails' directory]*

# Case study on 1T'-WTe<sub>2</sub>: DFT+U, multi-step approach



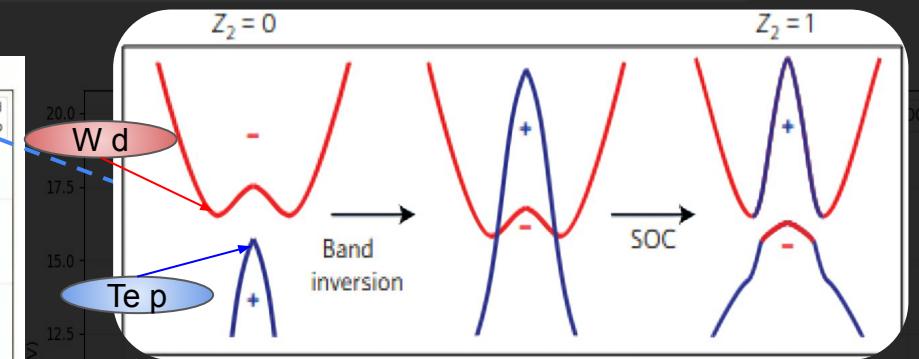
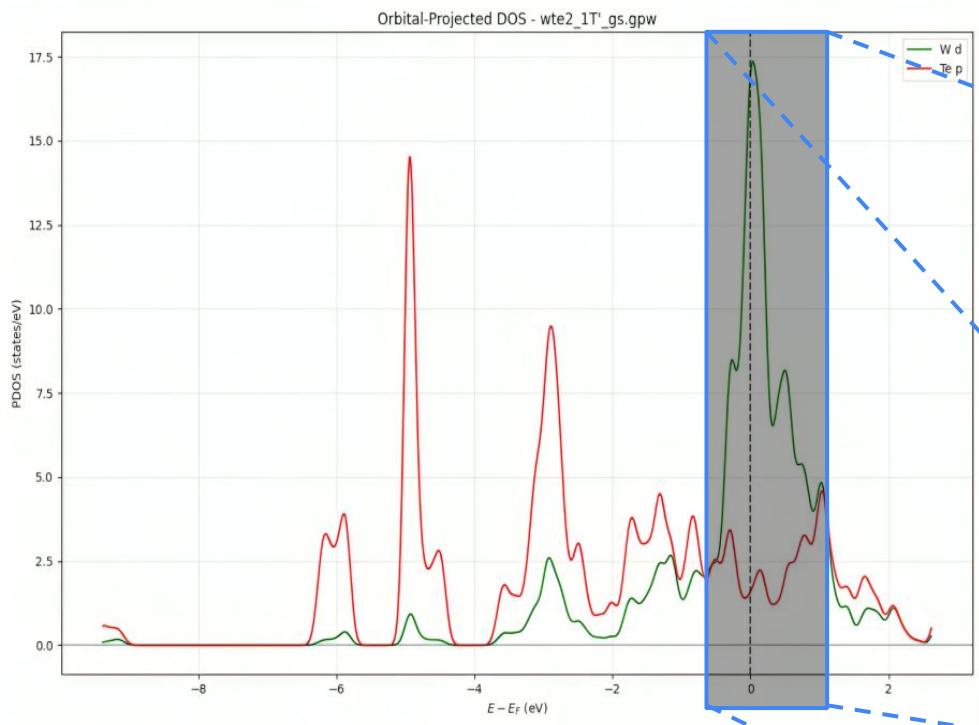
(\*)[Shujie Tang et al., Nature Physics **13**, 683–687 (2017)]

# Case study on 1T'-WTe<sub>2</sub>: DFT+U, multi-step approach

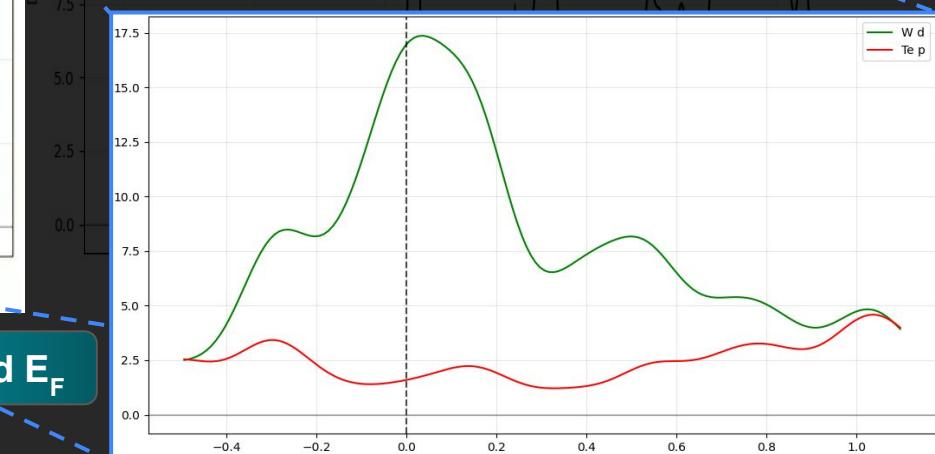


*Non-spin-polarized calculation*

# Case study on 1T'-WTe<sub>2</sub>: DFT+U, multi-step approach



Topologically trivial  $\rightarrow$  non-trivial  $\rightarrow$  SOC-splitting(\*)



Band Inversion: Reversal of orbital character around  $E_F$

(\*)[Shujie Tang et al., Nature Physics **13**, 683–687 (2017)]

# *Thank you for your attention!*

I am here because

I enjoy creating and presenting ideas.

**Contacts:**

[gv@materials.uoc.gr](mailto:gv@materials.uoc.gr) / [gv@csd.uoc.gr](mailto:gv@csd.uoc.gr)

[gv@iacm.forth.gr](mailto:gv@iacm.forth.gr) | FORTH/IACM-IESL

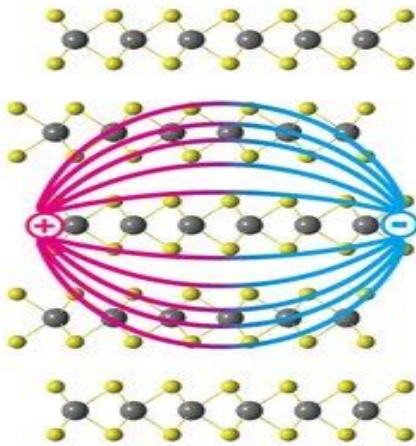
[Georgios Vourvachakis](#) | LinkedIn



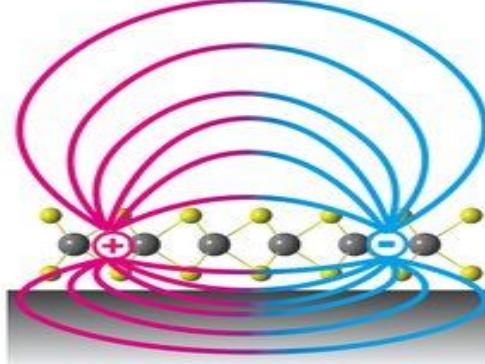
# Semiconducting Group-VI TMDs: $\text{MX}_2$ (M ∈ {Mo, W} and X ∈ {S, Se, Te})

## Dielectric screening of Coulomb interaction

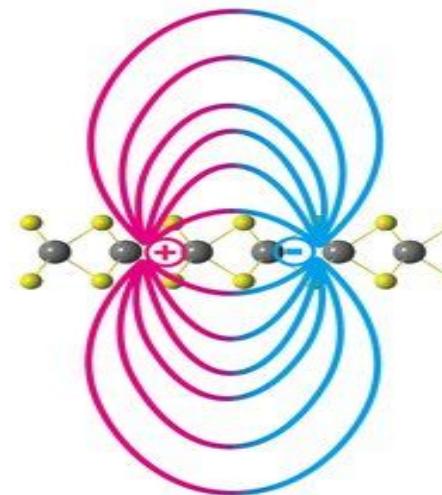
multilayer MoS<sub>2</sub>



monolayer MoS<sub>2</sub> + dielectric substrate



MoS<sub>2</sub> monolayer



**Screening:**  
Damping of electric fields due to the presence of mobile charge carriers.

[Chenxi Zhang et al.,  
Springer Nature **10(1)**  
(2020)]

Environmental Sensitivity of Coulomb interaction between charged particles inside the system.  
Notice the relative distances between charged particles and different ranges of electric field lines.

# Semiconducting Group-VI TMDs: $\text{MX}_2$ (M ∈ {Mo, W} and X ∈ {S, Se, Te})

Band gap of 2D TMDs (in eV), as obtained from first principle calculations.

[Roldán et al., AdP **526.9**, 347–357 (2014)]

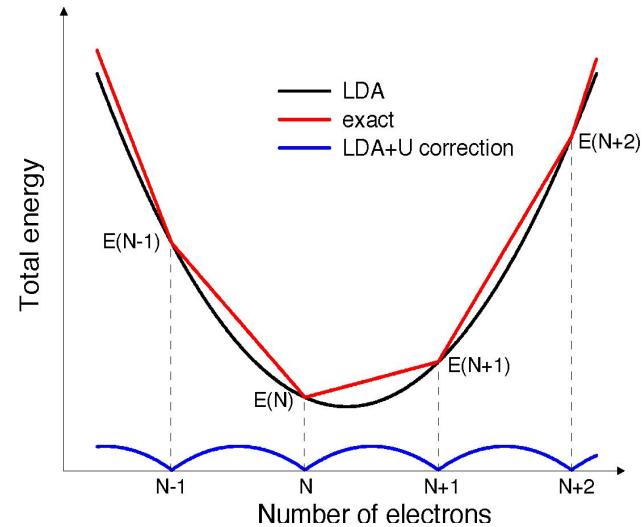
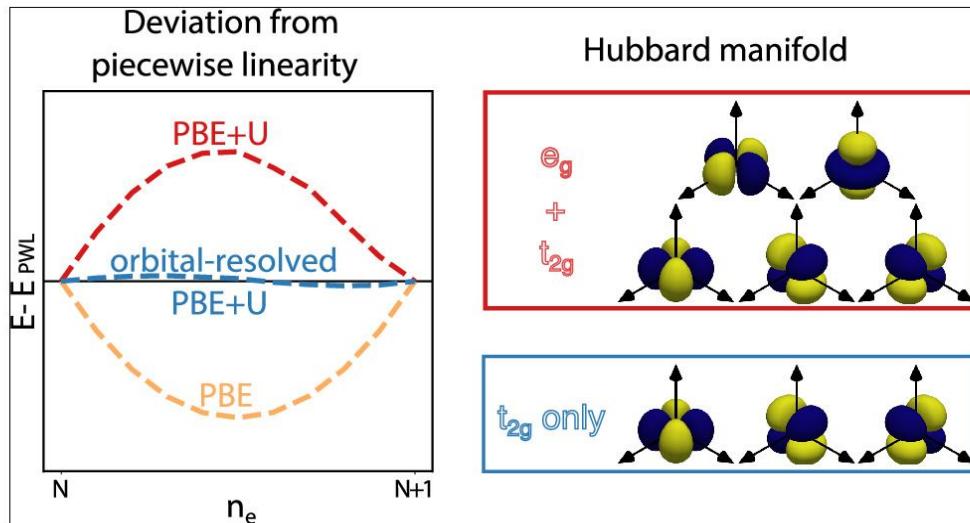
	Monolayer	Bilayer	Bulk
$\text{MoS}_2$	1.715	1.710–1.198	1.679–0.788
$\text{WS}_2$	1.659	1.658–1.338	1.636–0.917
$\text{MoSe}_2$	1.413	1.424–1.194	1.393–0.852
$\text{WSe}_2$	1.444	1.442–1.299	1.407–0.910
$\text{ReSe}_2$	1.43	—	1.35

Note: All monolayer samples present a direct gap. The two values given for bilayer and bulk samples for those compounds correspond to the sizes of the direct/indirect gaps, respectively.

# DFT+U: Orbital-Resolved Hubbard Parameters

$$E_{\text{DFT+U}} = E_{\text{DFT}} + \sum_a \frac{U_{\text{eff}}}{2} \text{Tr}(\rho^a - \rho^a \rho^a)$$

atomic orbital occupation matrix.



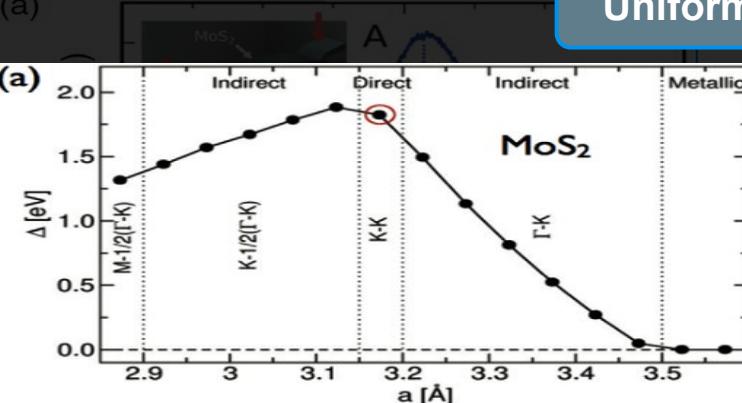
DFT+U is to treat the strong on-site Coulomb interaction of localized electrons, which is not correctly described by LDA or GGA, with an additional Hubbard-like term (e.g., for **p localized orbitals**).

The strength of the on-site interactions are usually described by parameters **U (on site Coulomb)** and **J (on site exchange)**.

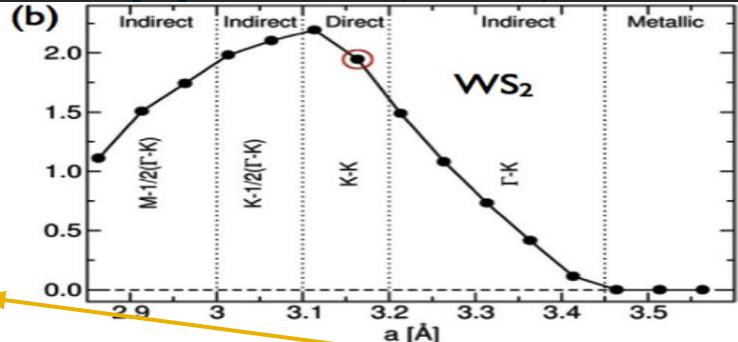
# Optoelectronic Strain Effects on Group-VI TMDs

## Uniform Isotropic Strain (DFT/PBE)

(a)



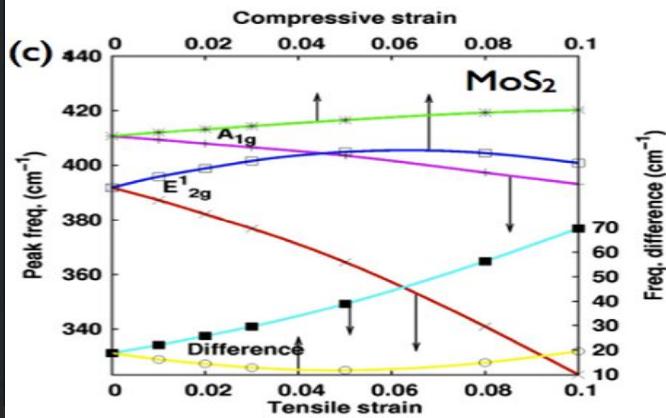
(b)



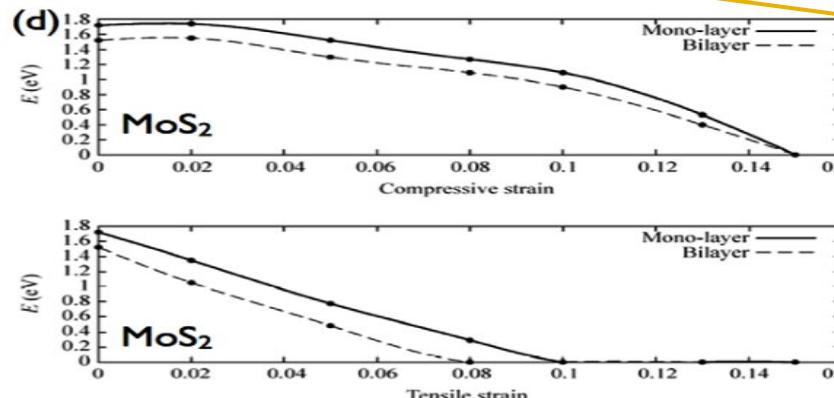
Tensile more pronounced than compressive strain

Reduction in band-gap

(c)



(d)



(d): [Suejeong et al., ACS Nano 7(8), 2013]