Why do we have unusual behavior in twisted bilayers of transition metal dichalcogenides?

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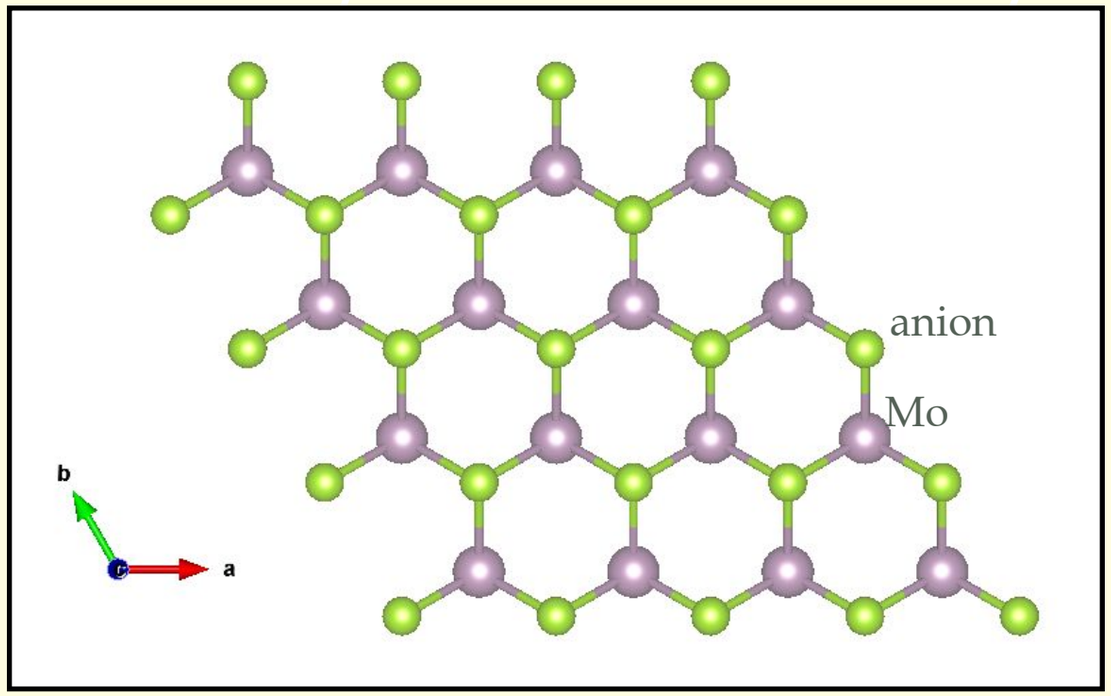
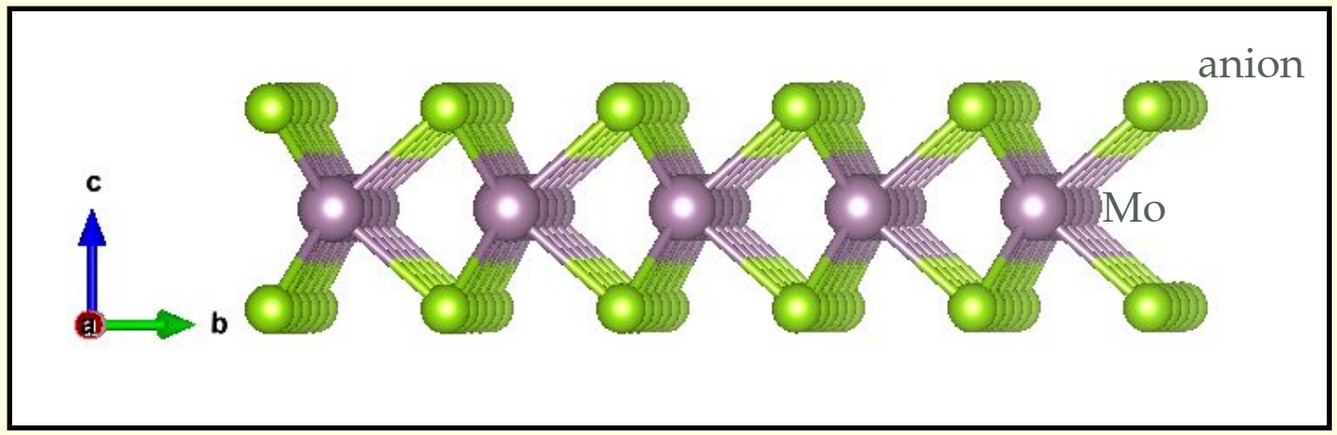
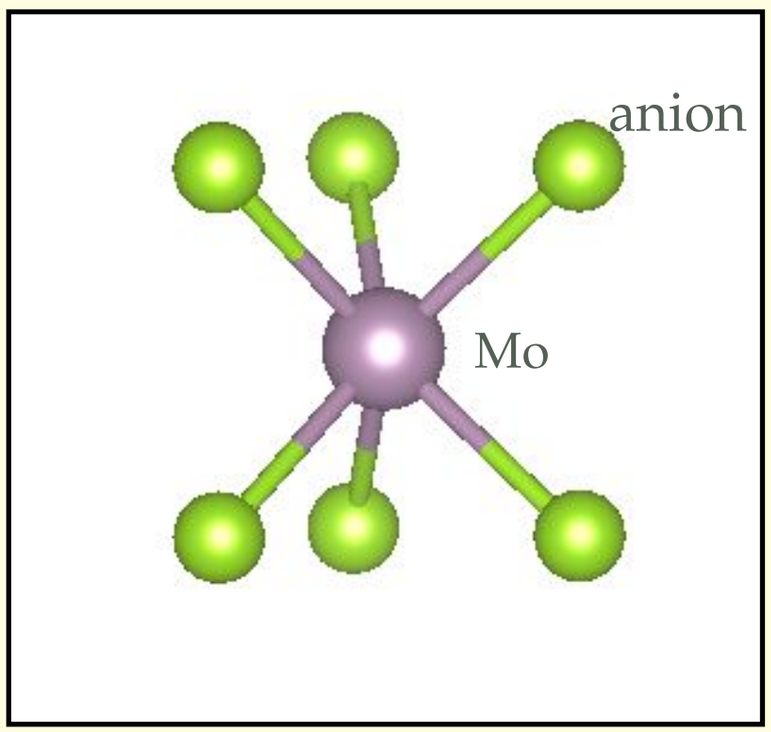
ICTS, July 2024.

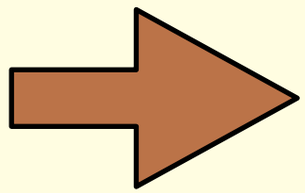
The TMDCs (Mo,W based) : Why are they semiconducting?



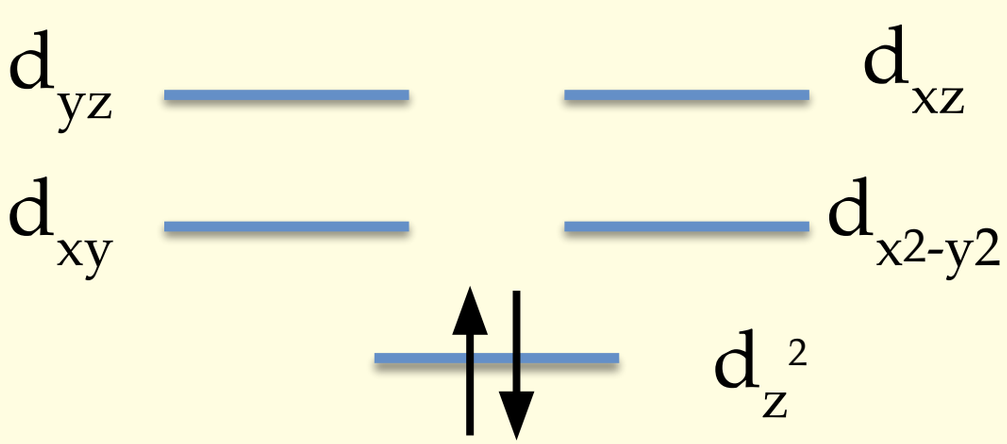
1H MoX_2



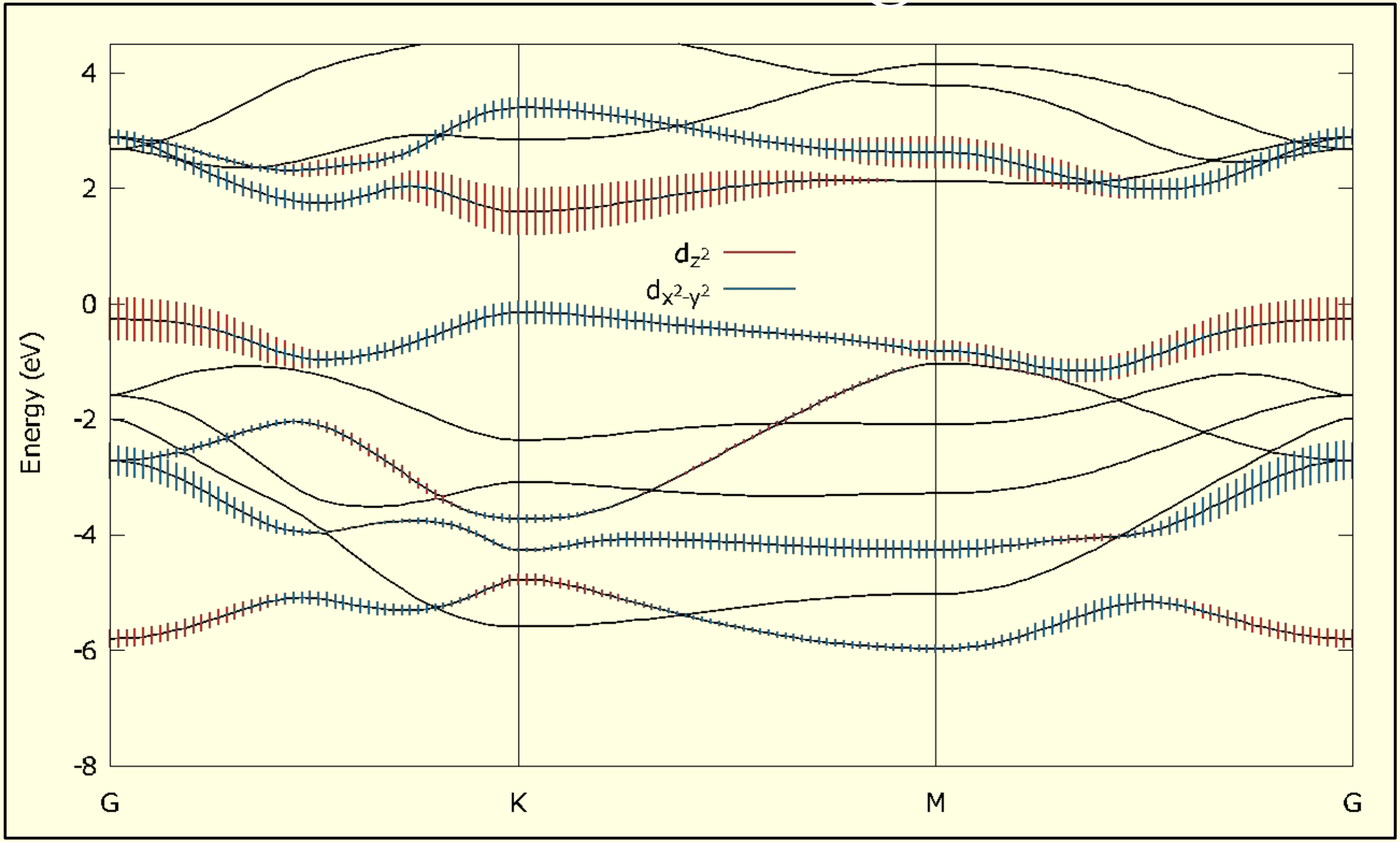




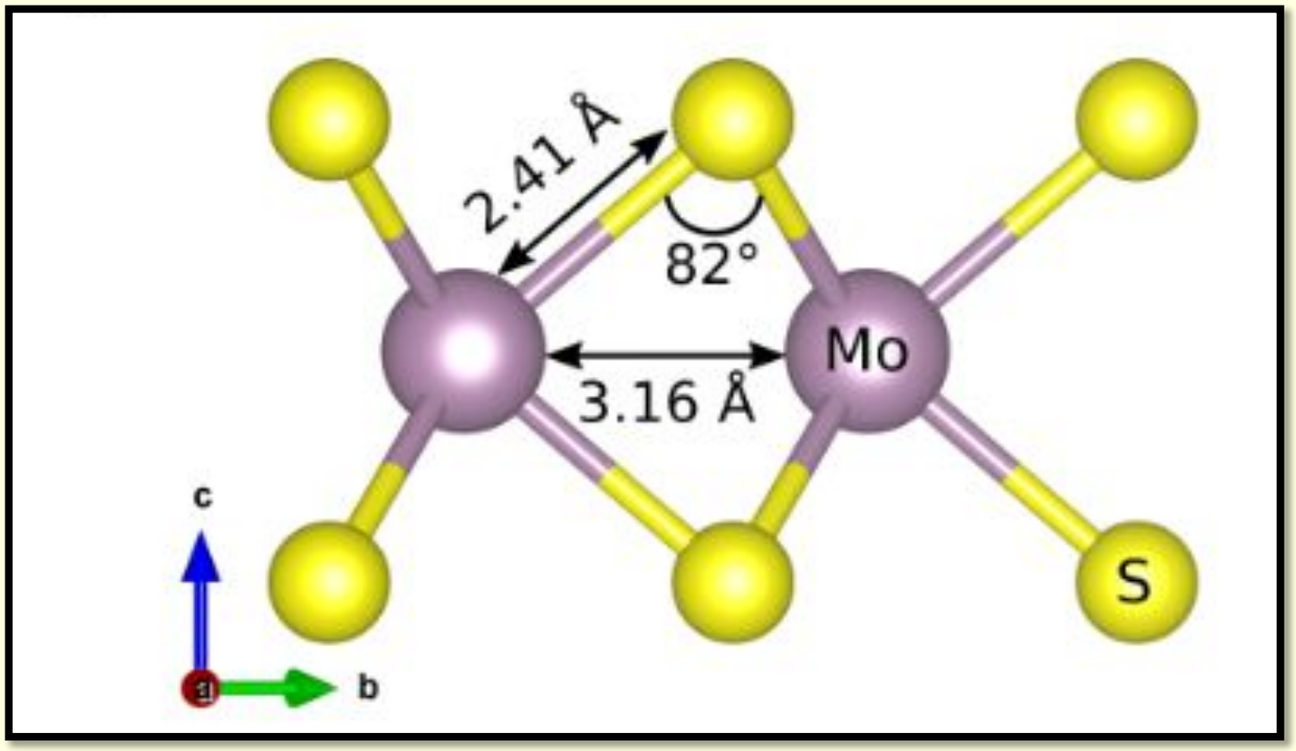
d-orbitals of Mo



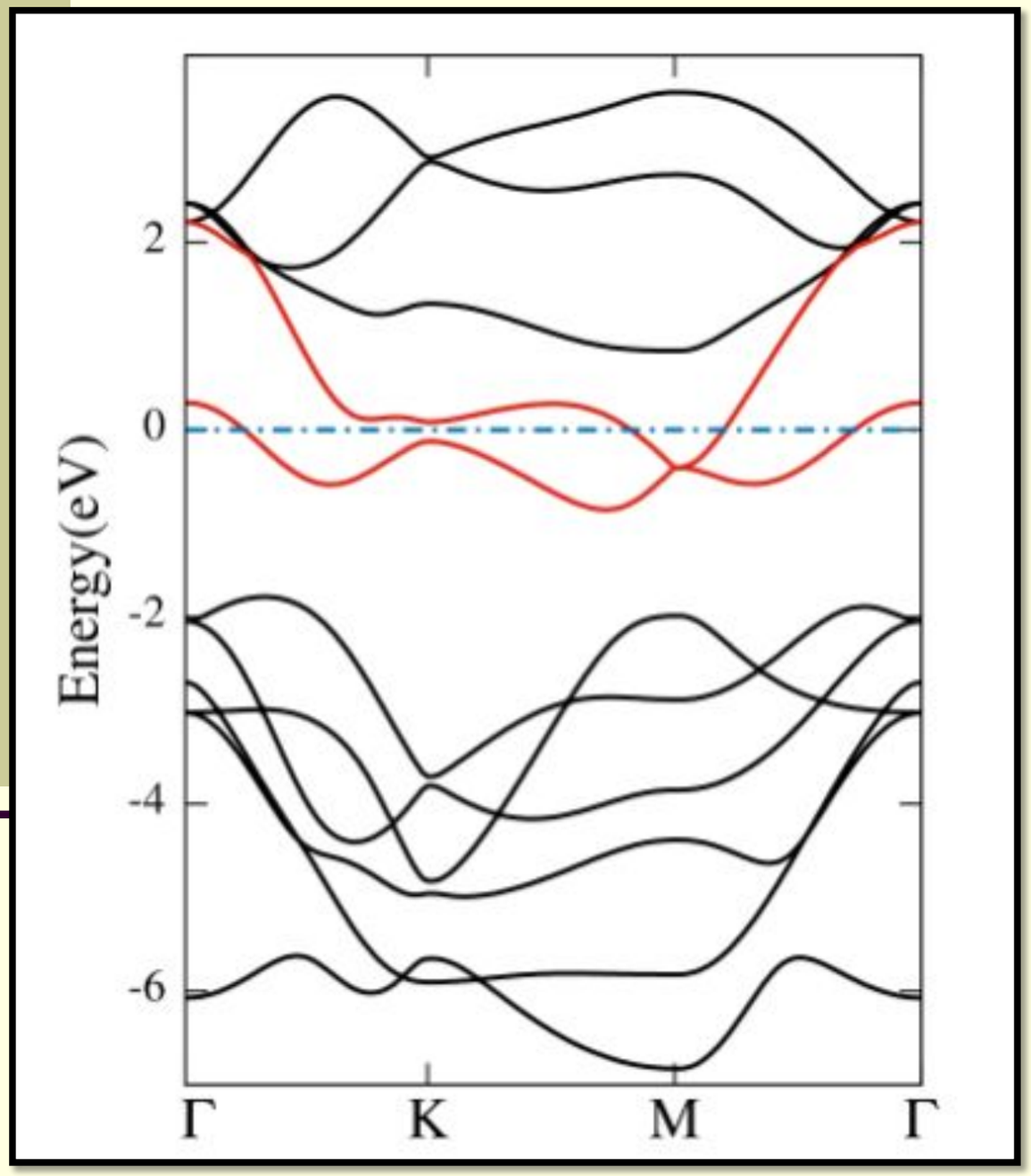
Do we understand the semiconducting state?

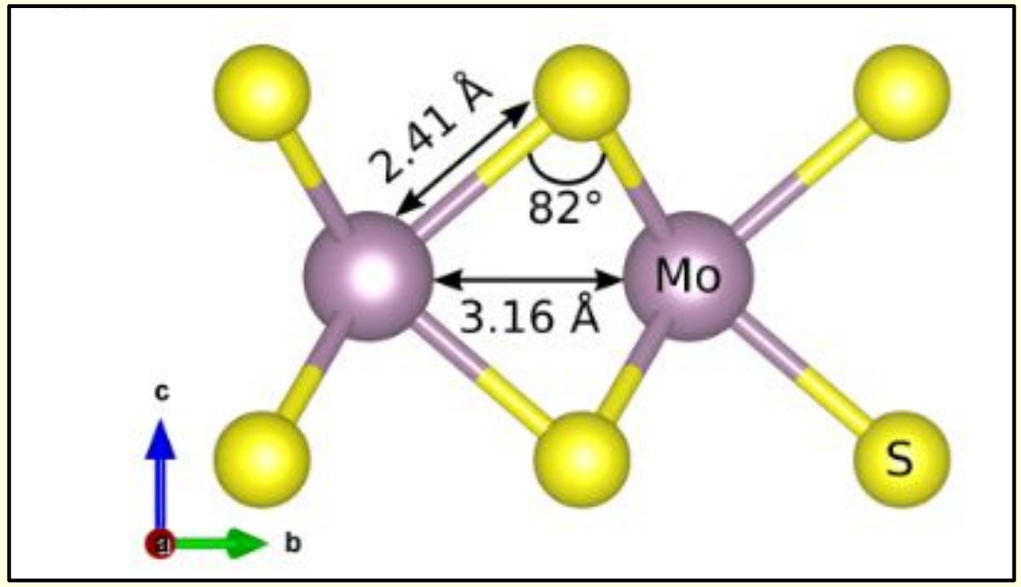


A quick look at the structure



Within a tight binding model





Switching off d-d interactions

SYSTEM IS METALLIC

What is the minimal model?

But a d-only model fails

Interaction between in plane orbitals

$$h_{12} = \left(\frac{3\sqrt{3}}{4}V_{dd\sigma} - \sqrt{3}V_{dd\pi} + \frac{\sqrt{3}}{4}V_{dd\delta}\right)\sin\alpha\sin\beta$$

$$\alpha = ak_x \text{ and } \beta = a\sqrt{3}k_y$$

At Γ : α = 0 and β = 0

At K : α = (2π)/3 and β = 2π

Both at Γ and K point, the in plane states remains degenerate!

reversal at G and K + the system remaining semiconducting?

d_{xy}, $d_{x^2-y^2}$

d_{z^2}

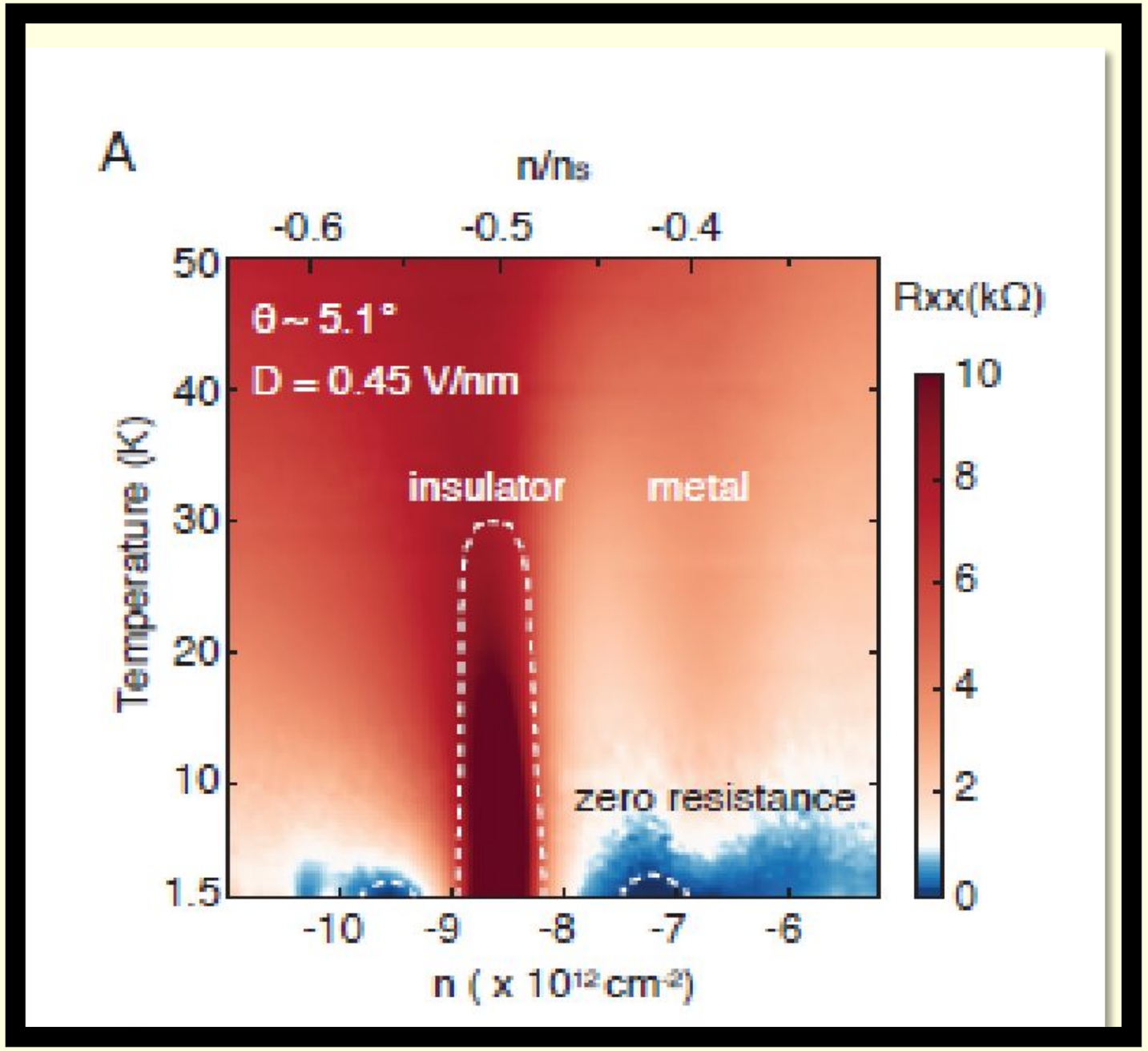
G

K

Coupling between in-plane orbitals is through the p orbitals

Moving on to the twisted limit

For twisted WSe_2



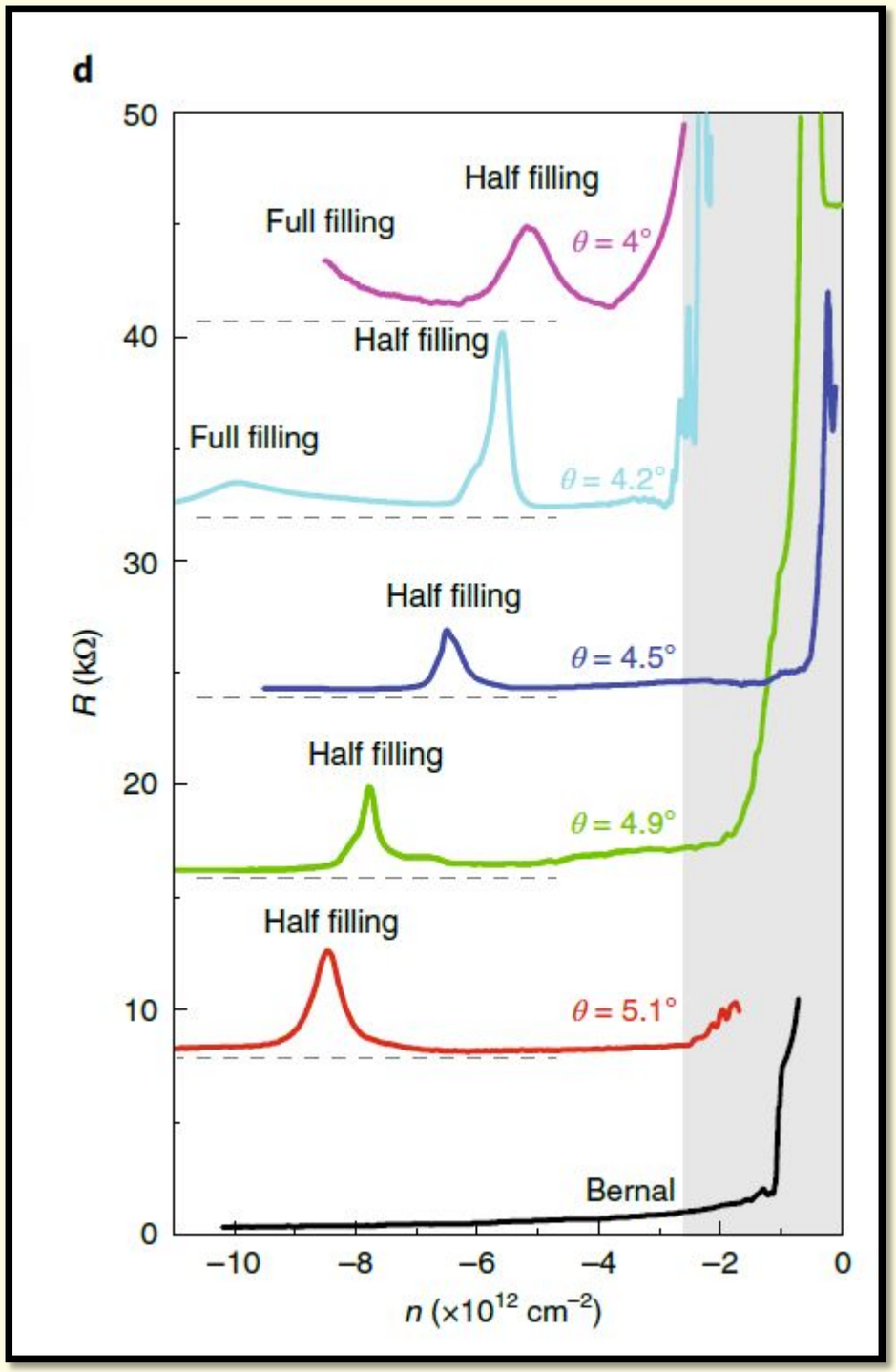
L. Wang et al., Nat. Materials 19, 861 (2020).

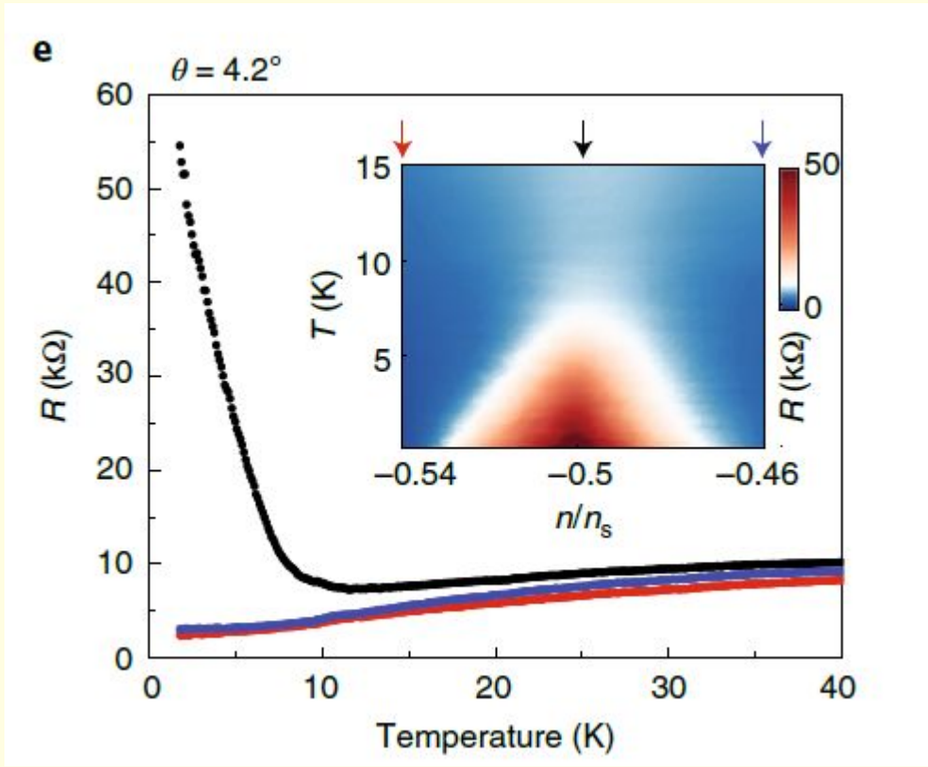
What does one expect?

Conduction band

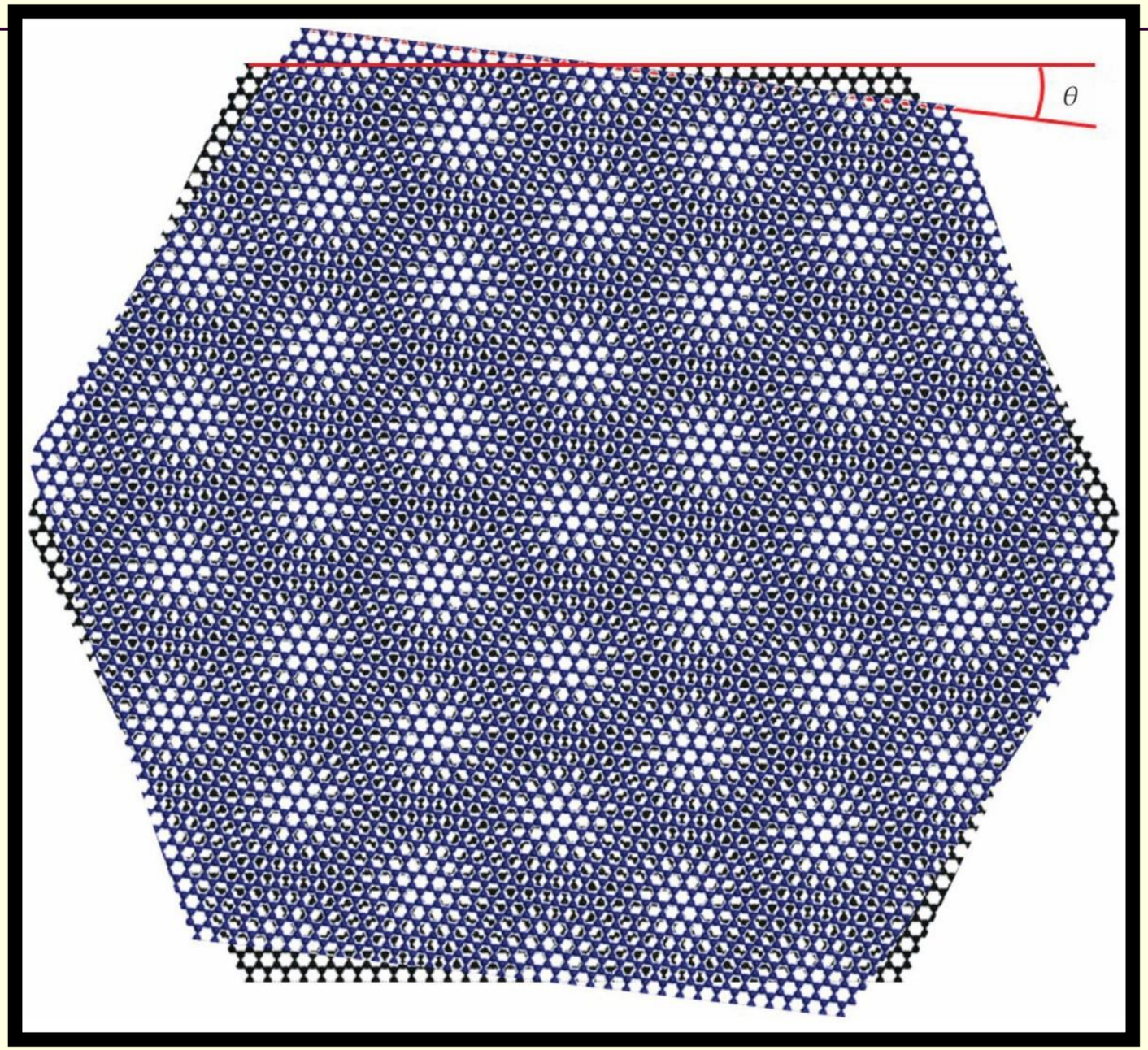
Valence band

For twisted WSe_2





The twisted bilayers :



Upper layer rotated slightly with respect to the lower layer.

This leads to

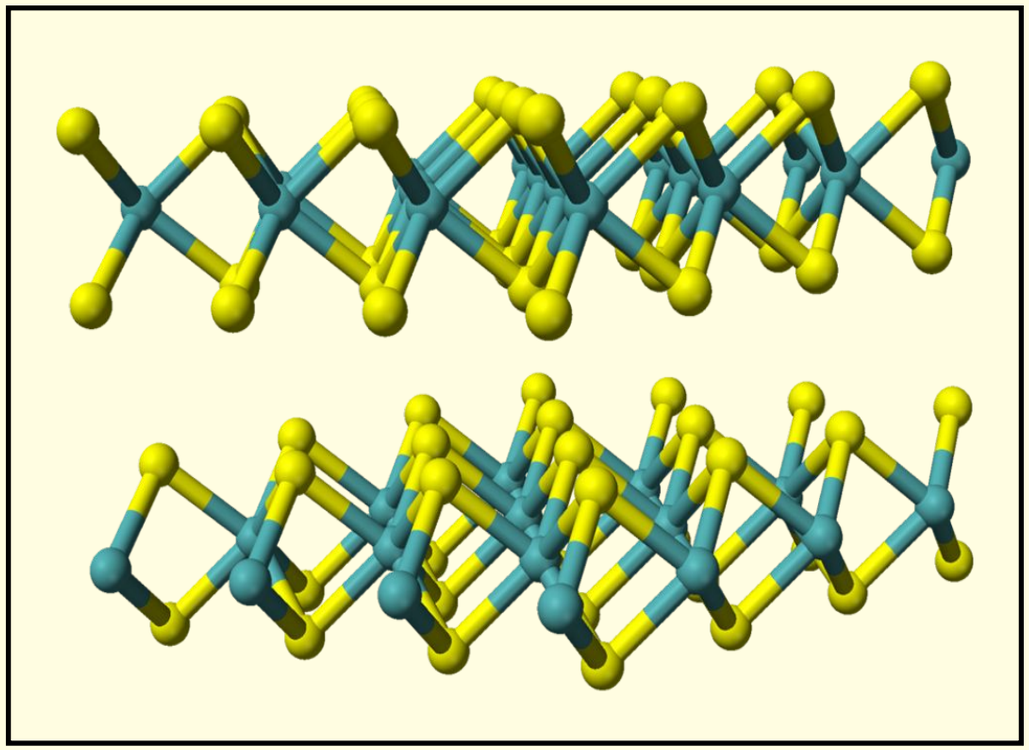
large unit cells

small Brillouin zones

Should we think of these as giant molecules with dispersionless levels?

H.M. Hill, Physics Today 73 1 (2020).

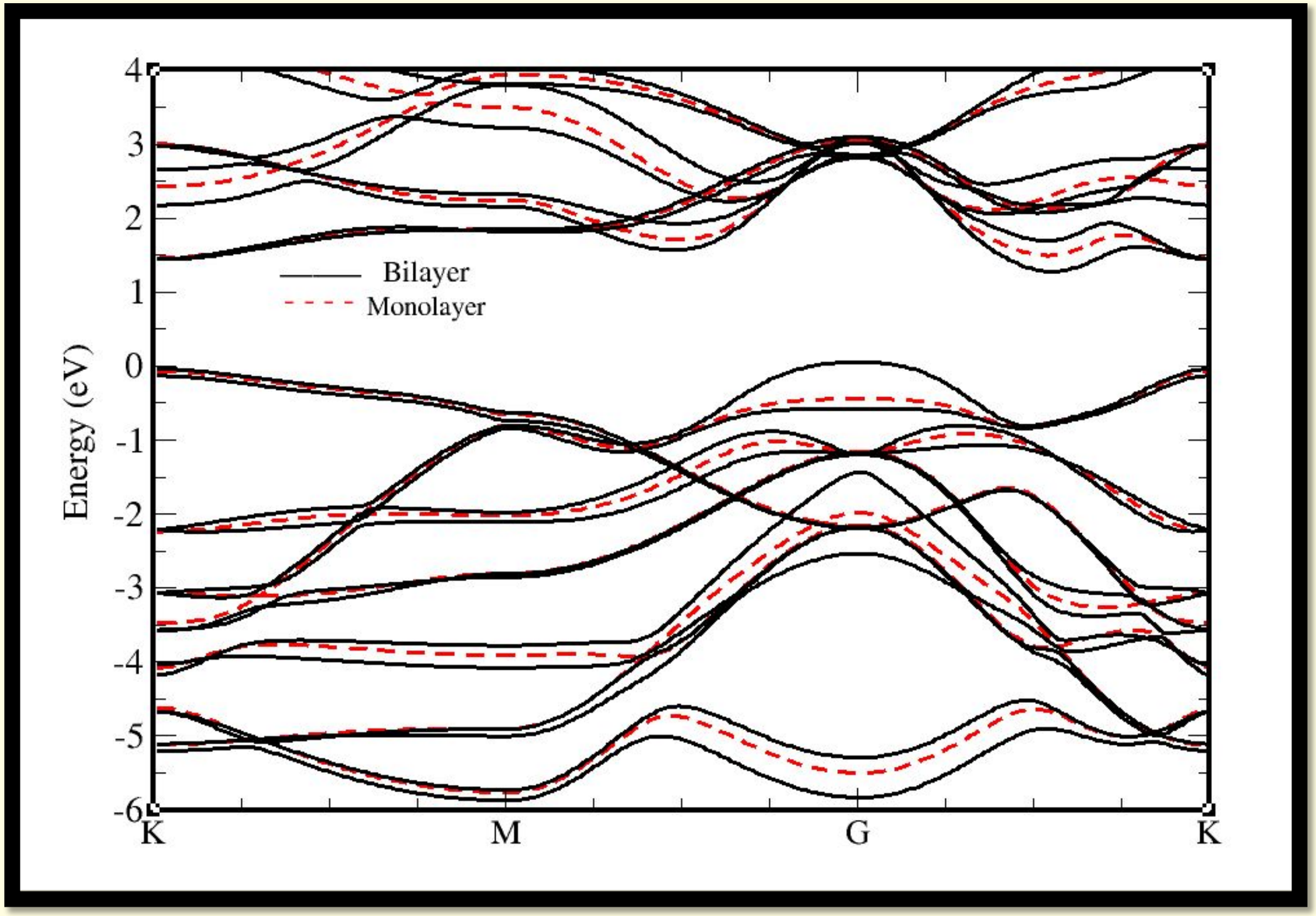
What do we know about the untwisted bilayers?



Most popular technique to separate them is the "scotch-tape" technique.

Implying a weak interaction between the layers.

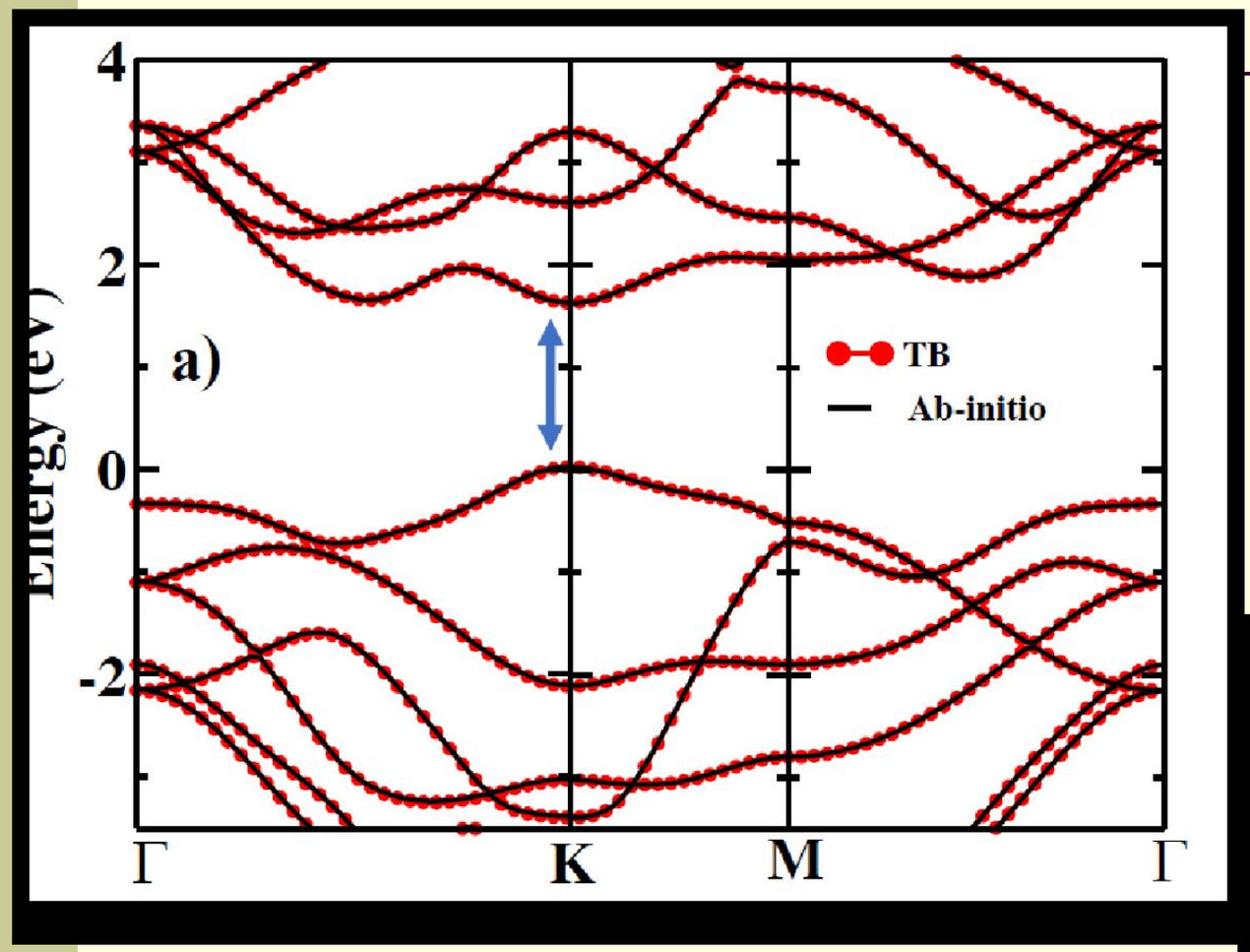
Consequences of a weak coupling between the layers



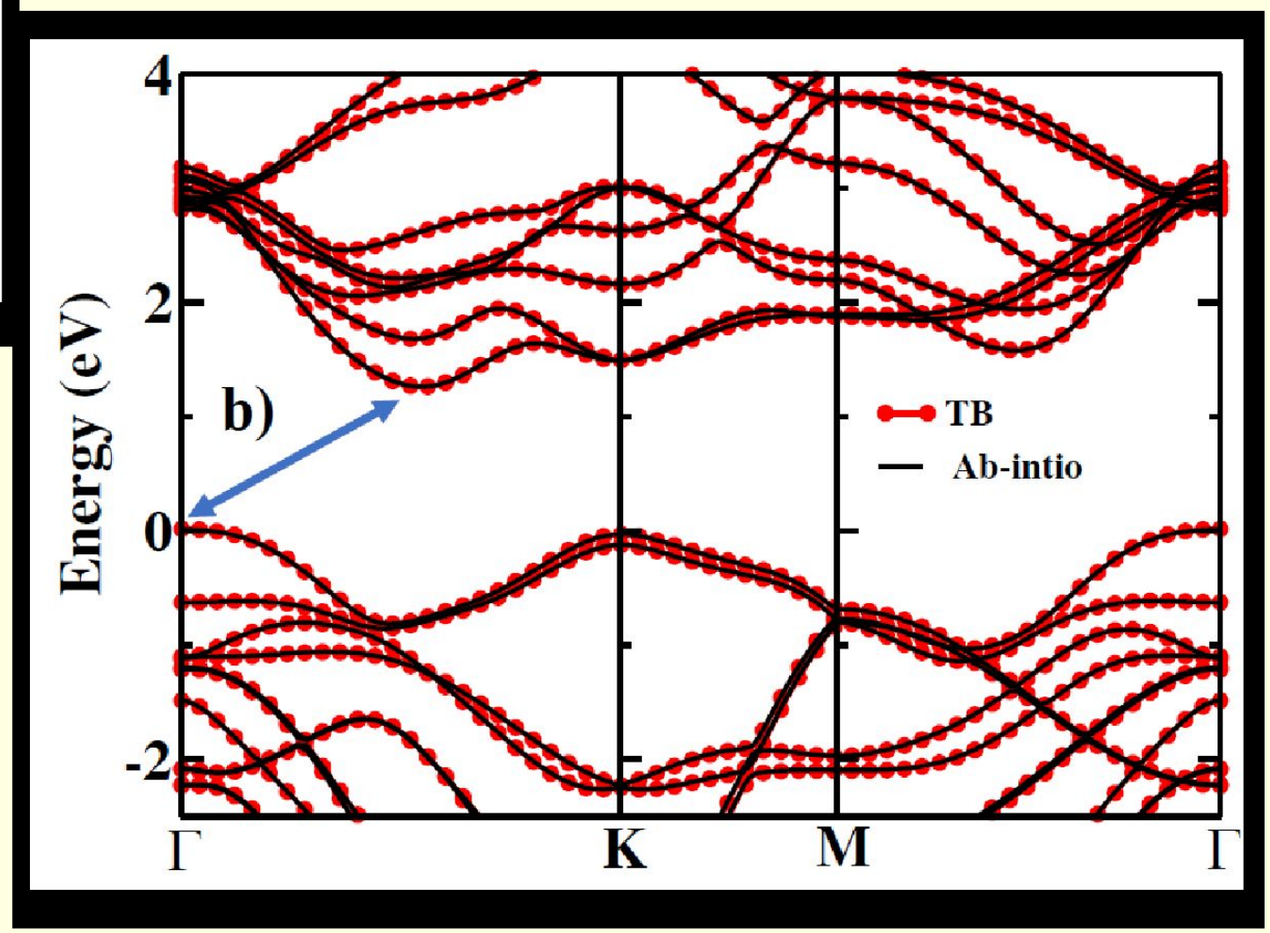
Suggesting a weak perturbation of the monolayer band structure.

Why do we see changes?

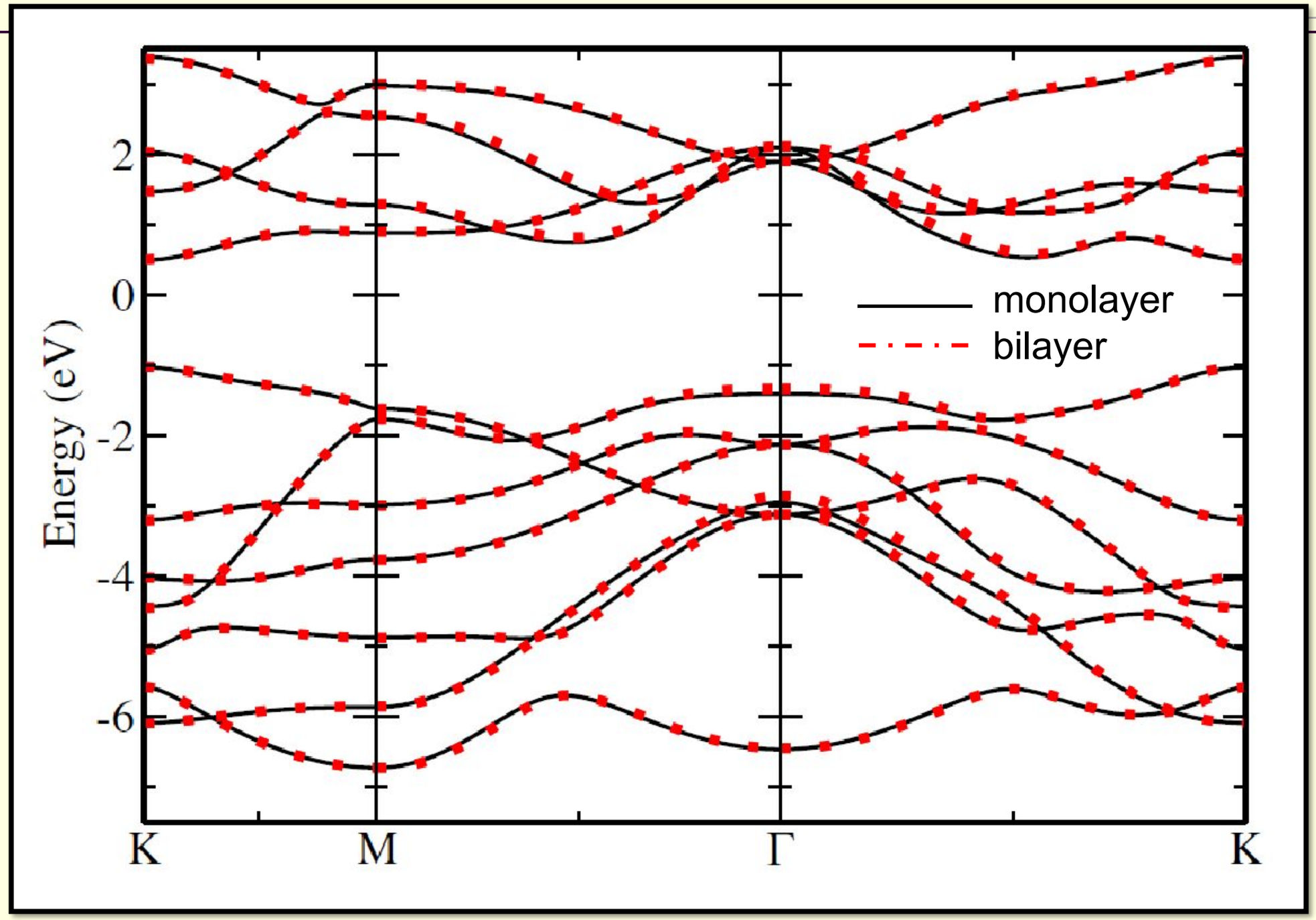
Monolayer



Bilayer



Bilayer band structure with interlayer interactions switched off, superposed on monolayer



So how should we view the Moire unit cells?

Untwisted limit + a weak perturbation

First introduced by us in

P. Kumari, J. Chatterjee and P. Mahadevan, Phys. Rev. B 045432 (2020).

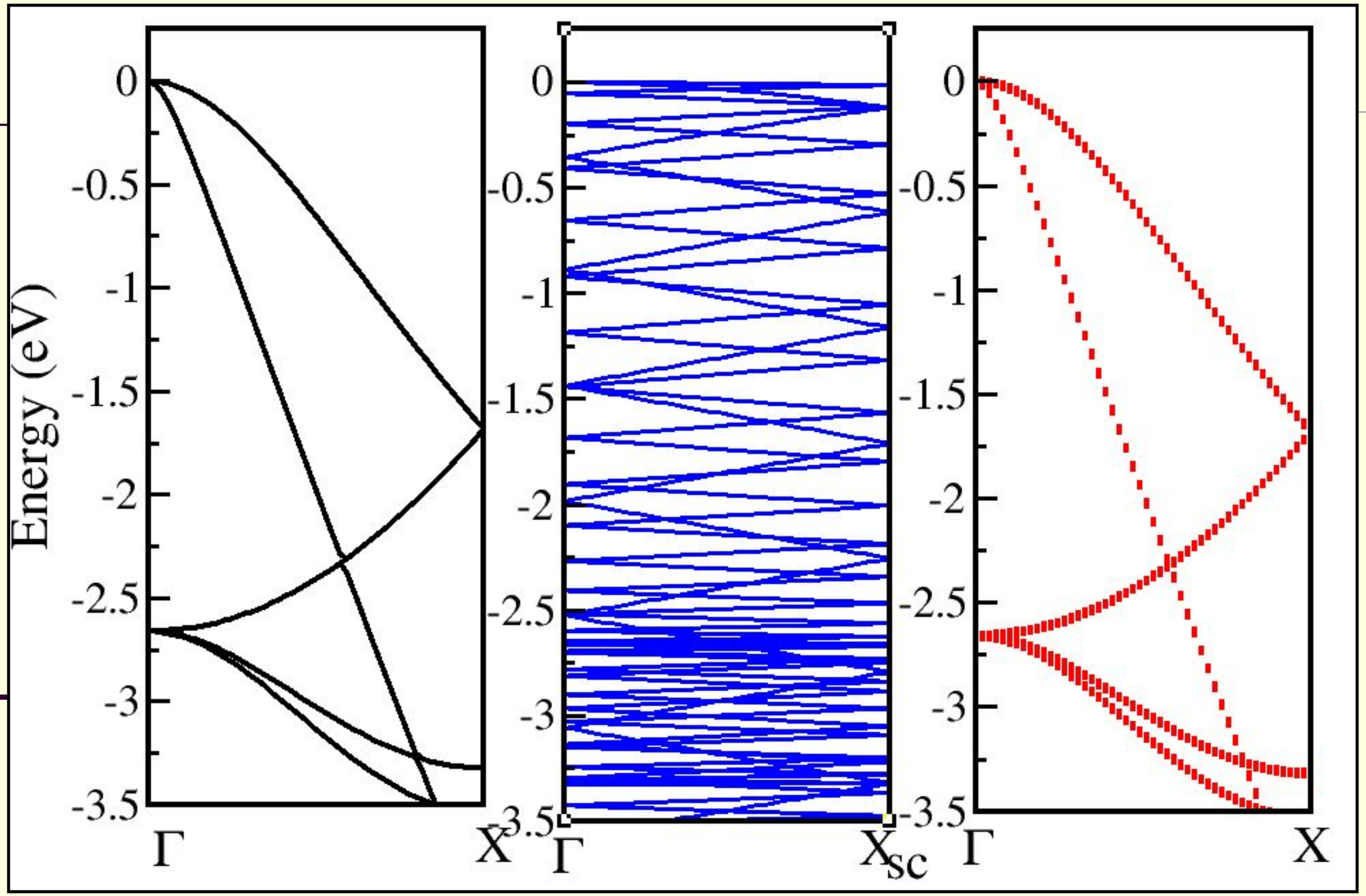
How should we recover the primitive cell limit?

- .

$$P_{\vec{K}m}(\vec{k}_i) = \sum_n \left|\langle \vec{K}m | \vec{k}_i n \rangle\right|^2$$

$$P_{\vec{K}m}(\vec{k}_i) = \sum_{\vec{g}} \left| C_{\vec{K}m}(\vec{g} + \vec{k}_i - \vec{K}) \right|^2$$

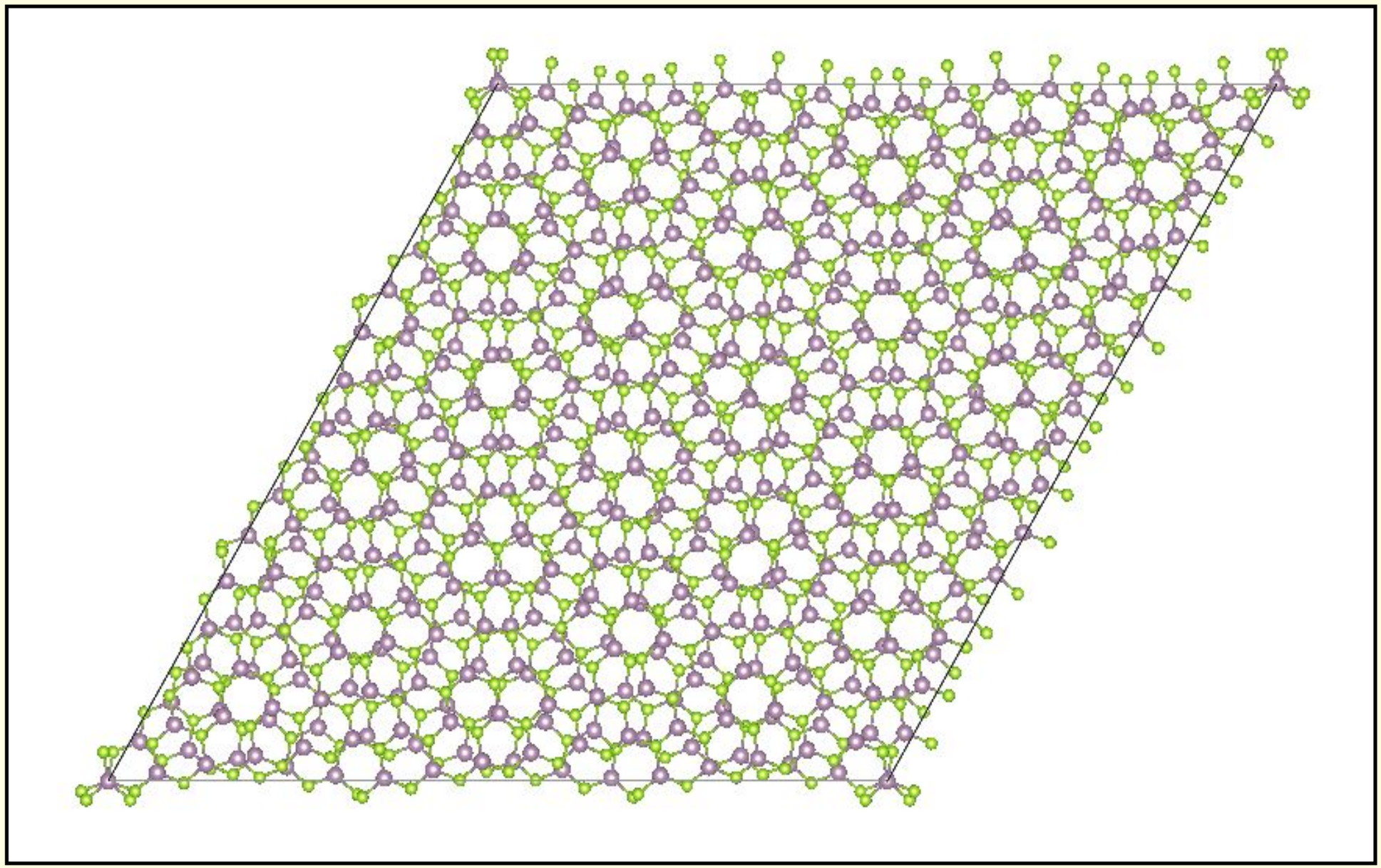
V. Popescu and A. Zunger, Phys. Rev. B 85, 085201 (2012).



Primitive cell

Super cell

Twisted bilayer of $MoSe_2$ at 19.03^{o}



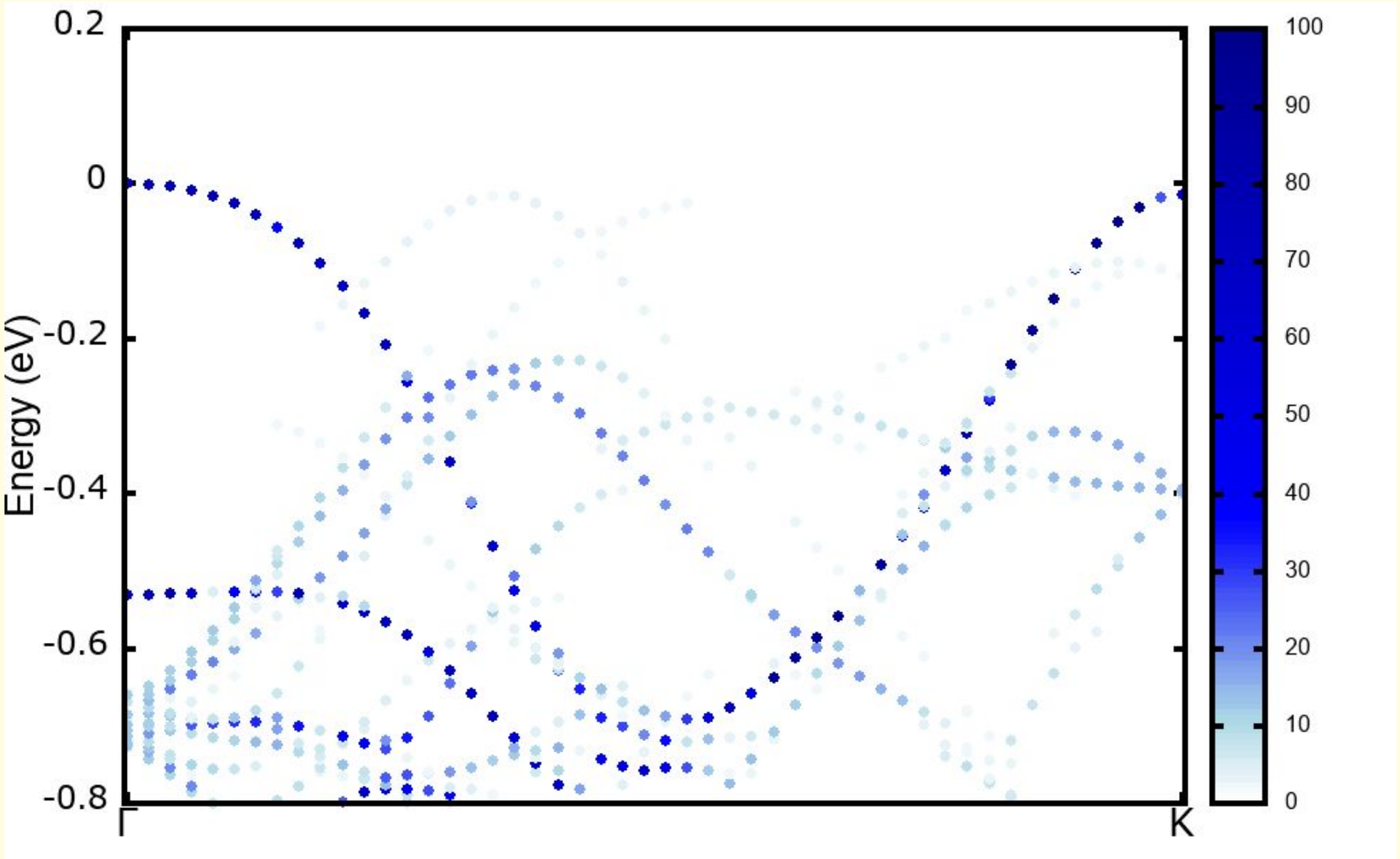
No of atoms=1482
Unit cell dimensions ~ 51.69 A 16 x primitive unit cell

S. Patra, P. Kumari, and P. Mahadevan, Phys. Rev. B 102, 205415 (2020)

Along the Moire cell direction

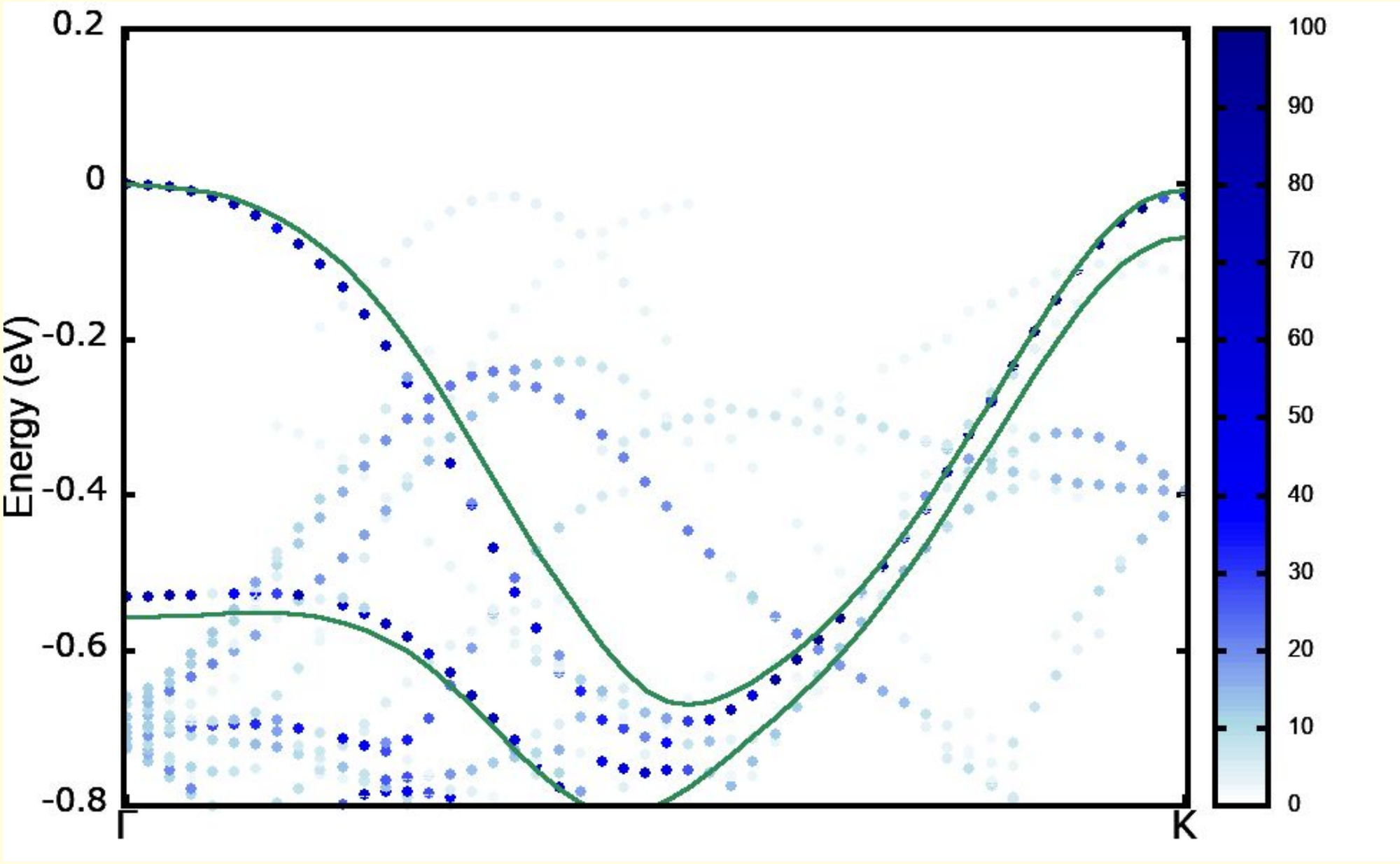
S. Patra, M. Das, and P. Mahadevan, J. Phys. Materials (in press).

Along the primitive cell directions



S. Patra, P. Kumari, and P. Mahadevan, Phys. Rev. B 102, 205415 (2020)

Comparison with the unperturbed band structure

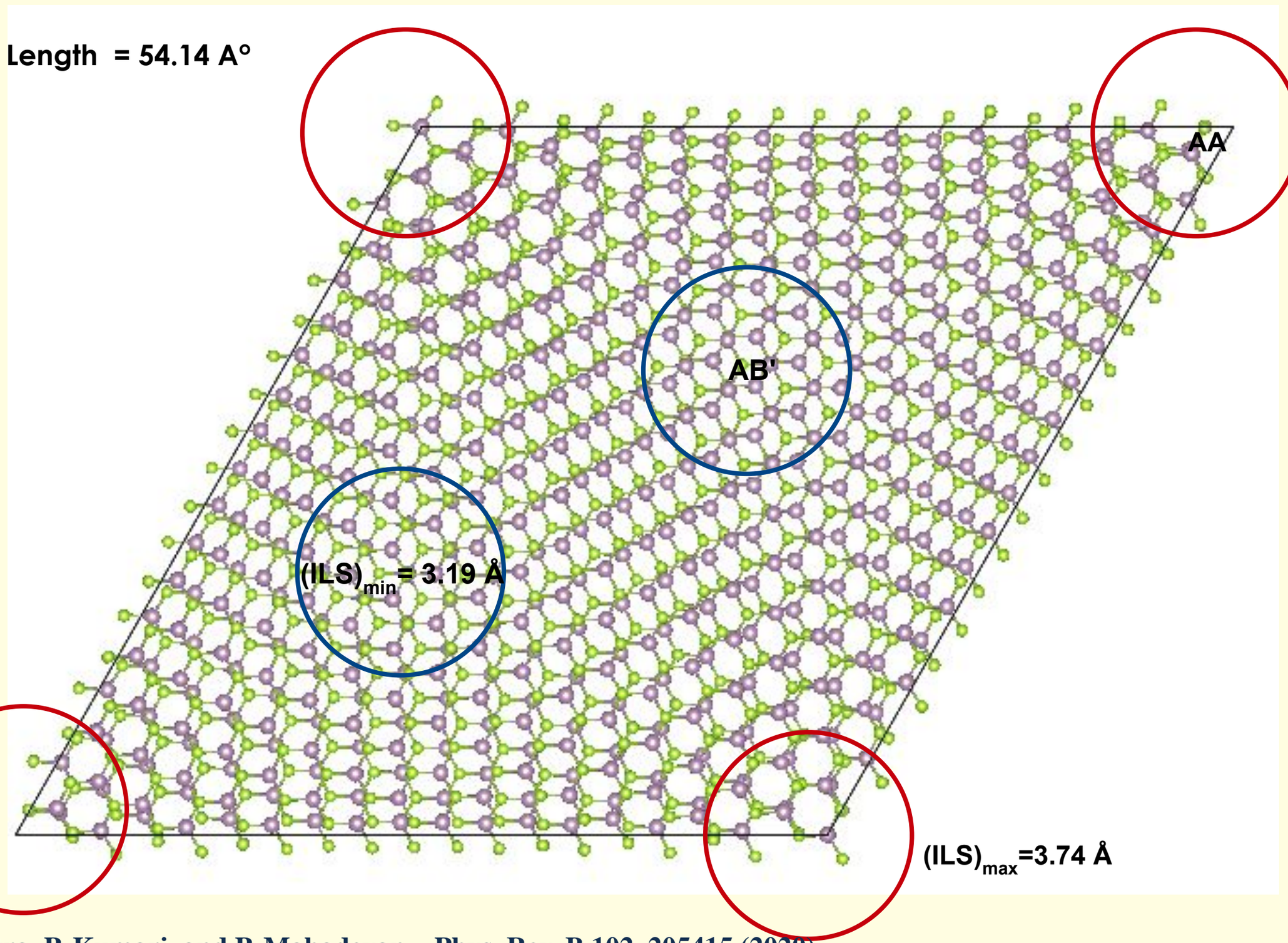


The low energy band structure is very weakly perturbed.

S. Patra, P. Kumari, and P. Mahadevan, Phys. Rev. B 102, 205415 (2020)

So is the low energy electronic structure always similar to the untwisted limit?

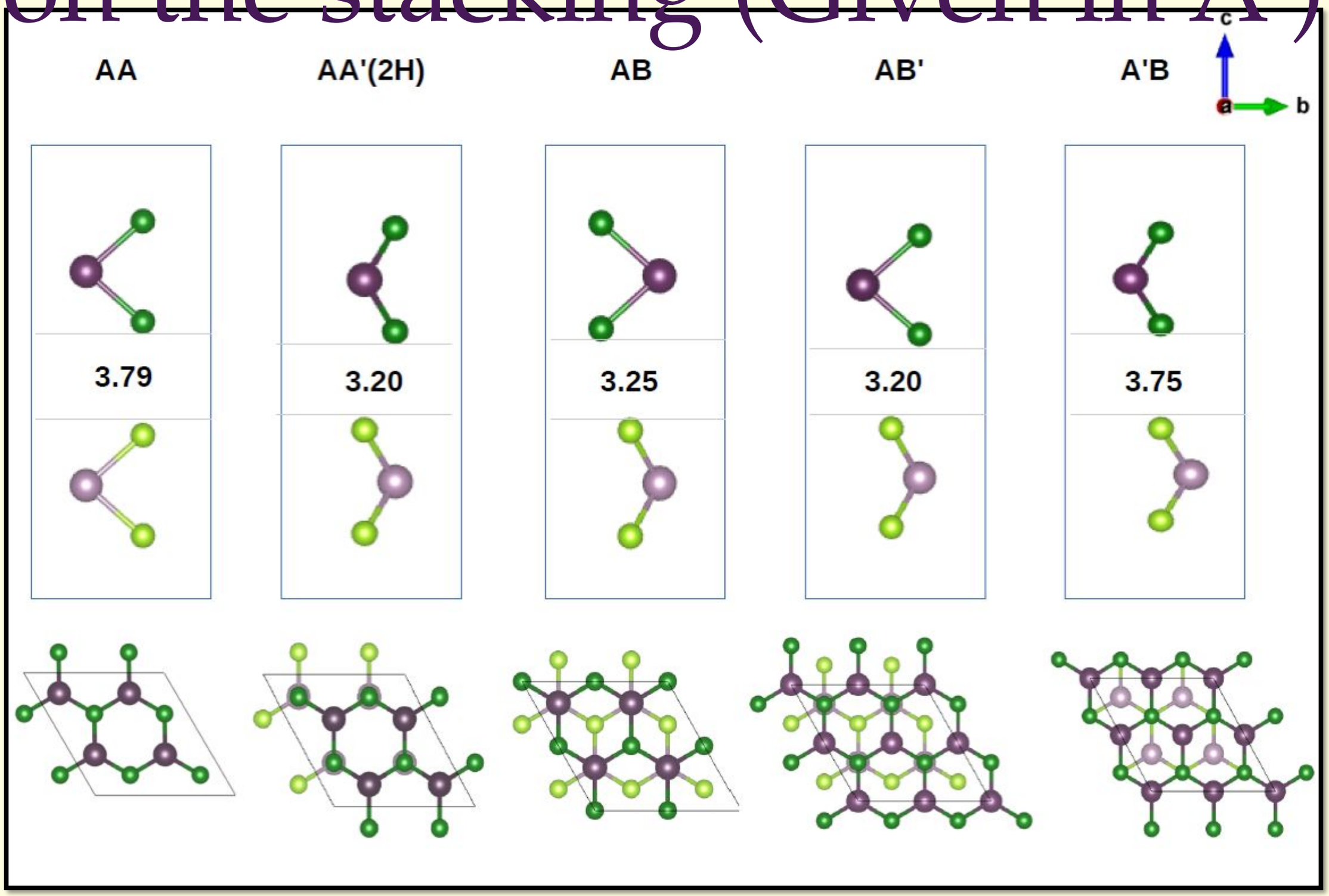
Twisted bilayer of $MoSe_2$ at 3.48^{o}



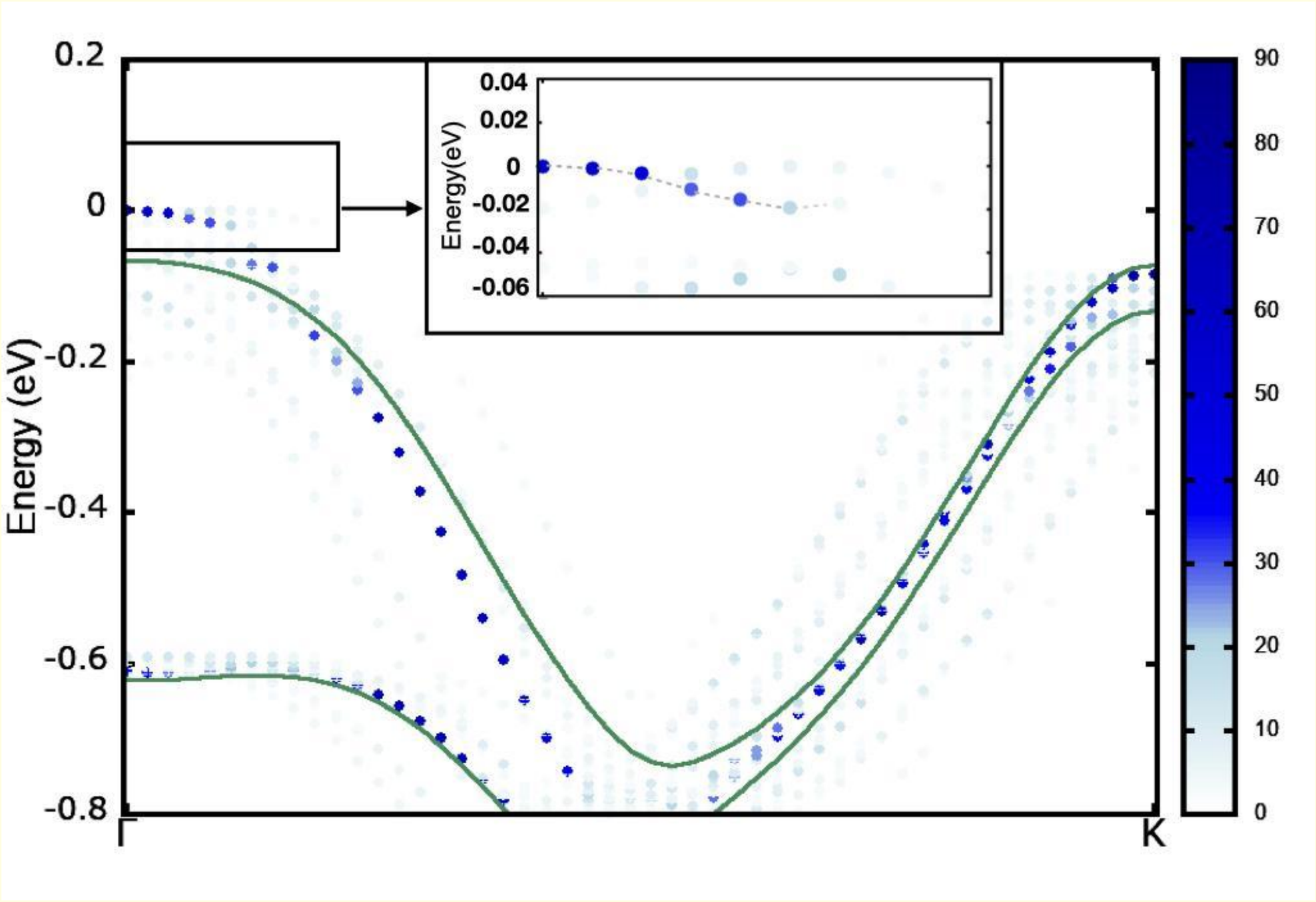
S. Patra, P. Kumari, and P. Mahadevan, Phys. Rev. B 102, 205415 (2020)

Different types of primitive cell stacking:

Interlayer distance depends on the stacking (Given in Å)



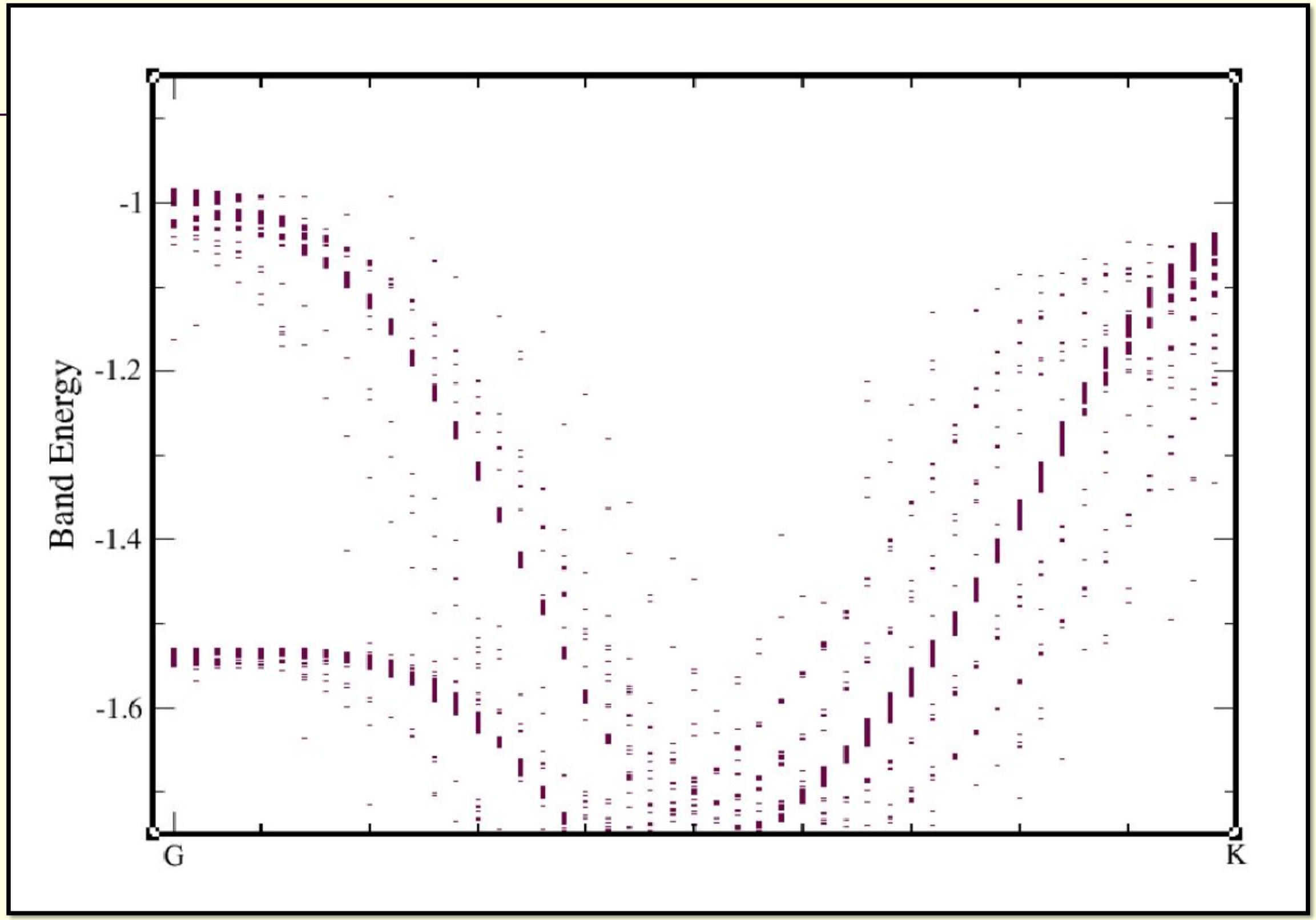
Along the primitive cell directions



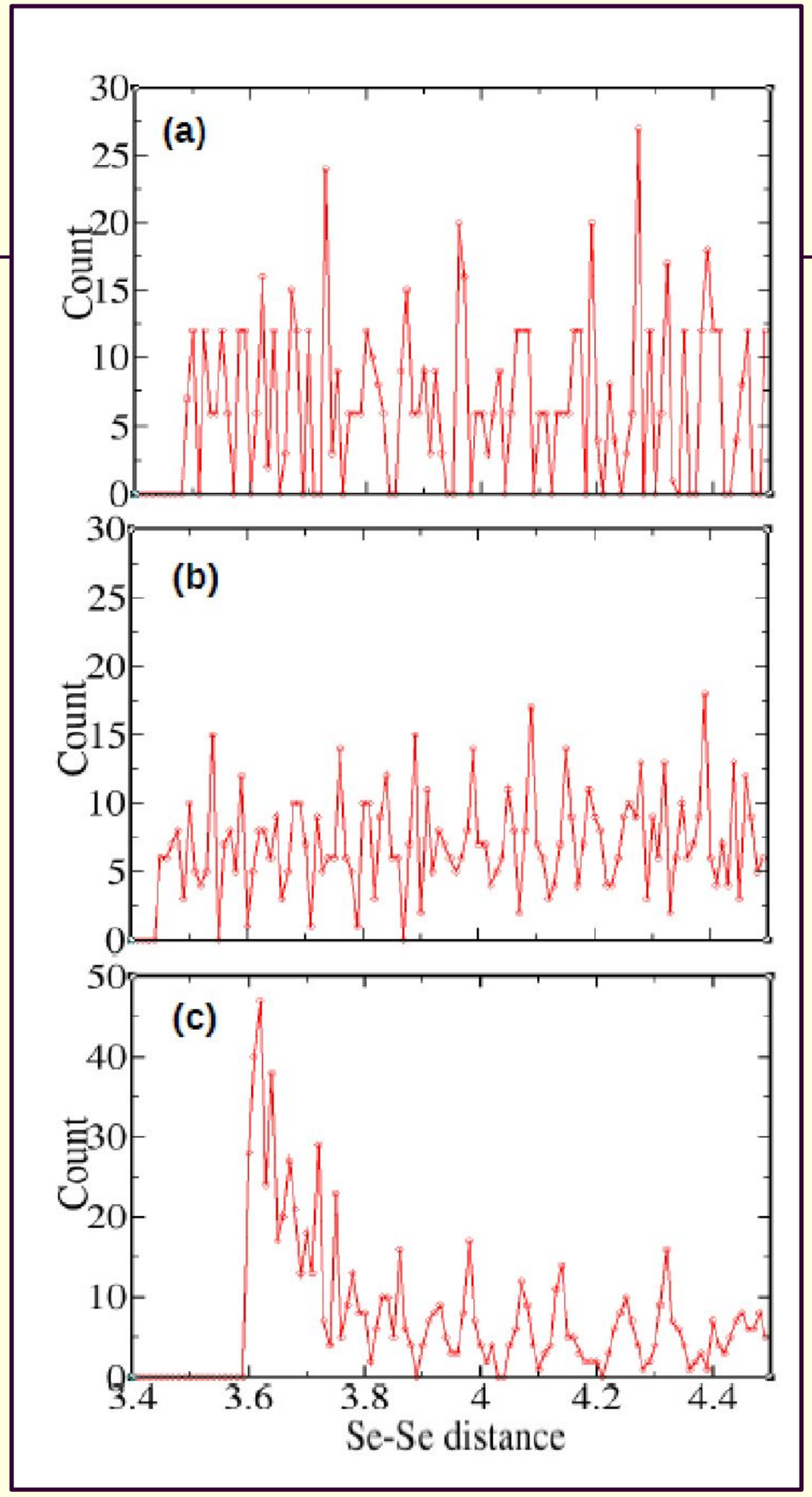
Split off band has a width of 19 meV

S. Patra, P. Kumari, and P. Mahadevan, Phys. Rev. B 102, 205415 (2020)

At a fixed interlayer separation of 3.44 A°



Interlayer Se-Se distances



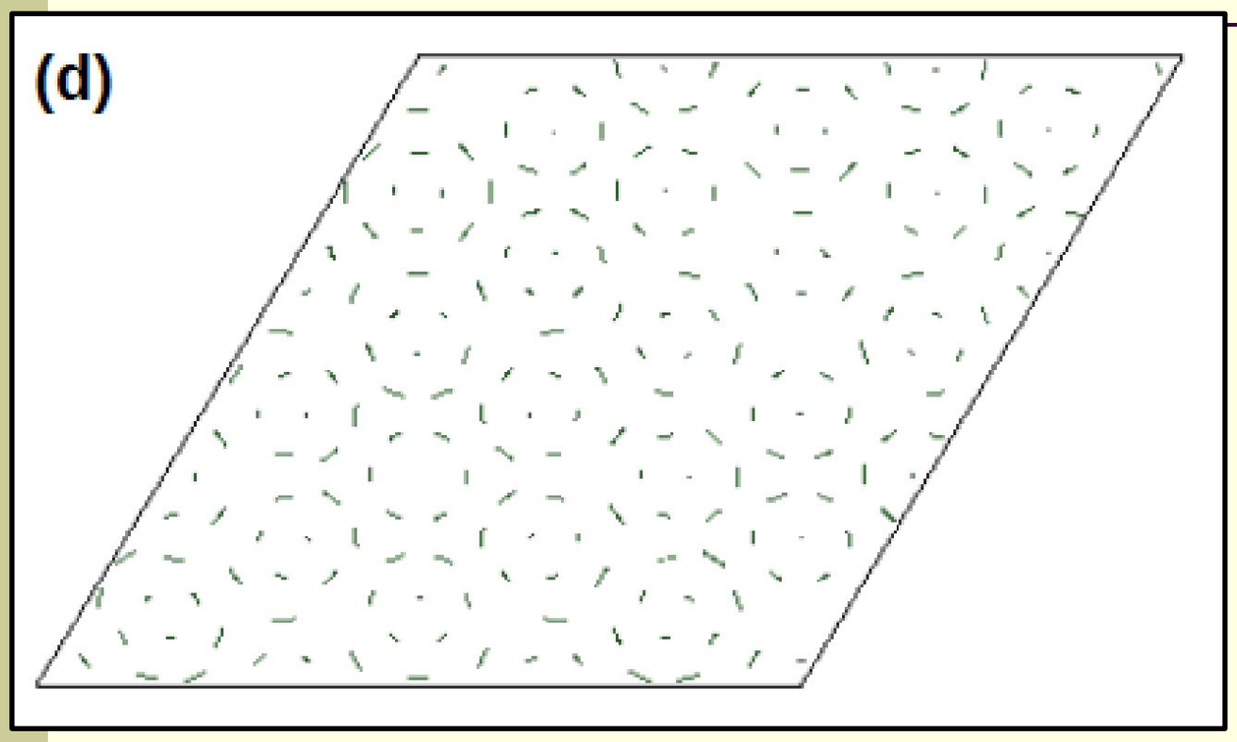
19.03°

3.48° at fixed interlayer separation

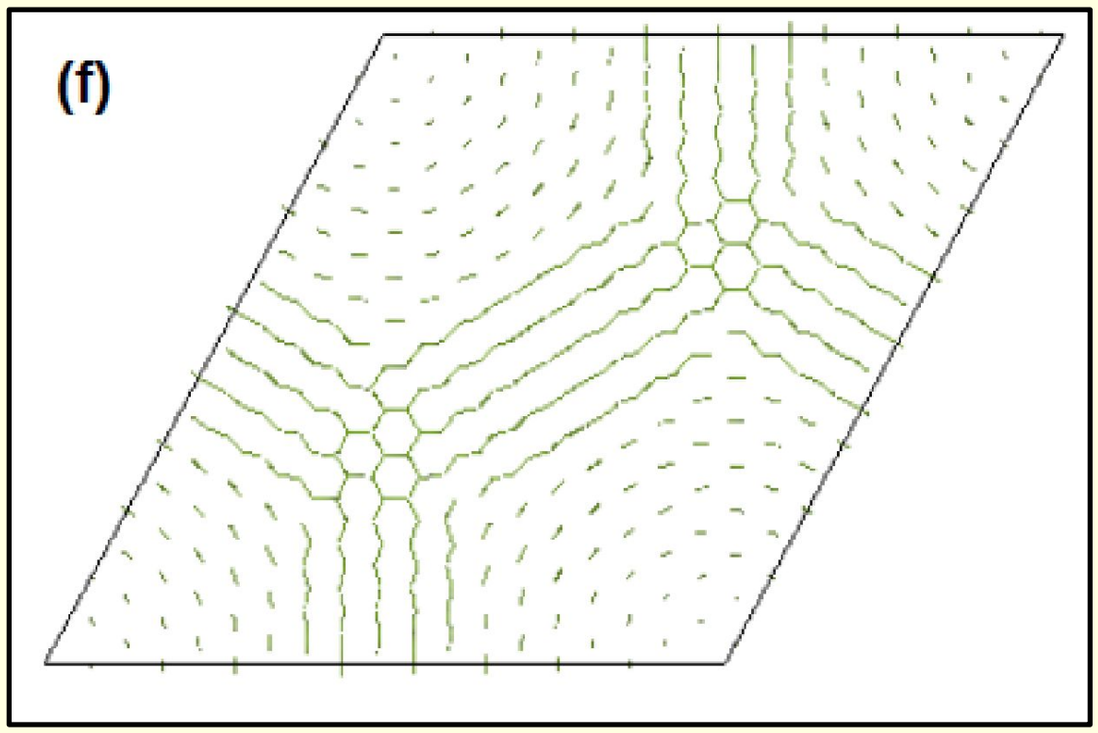
3.48° with interlayer separation optimised

Shortest set of Se-Se distances < 3.8 A°

At 19.03° with optimised structure

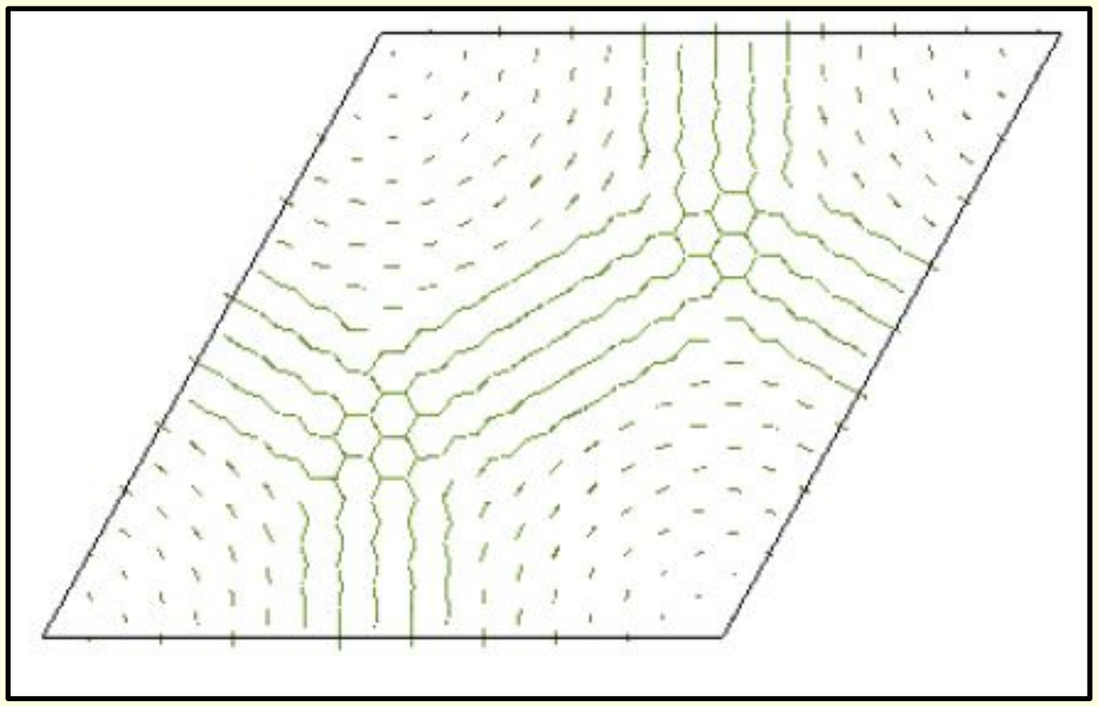


At 3.48° with optimised structure

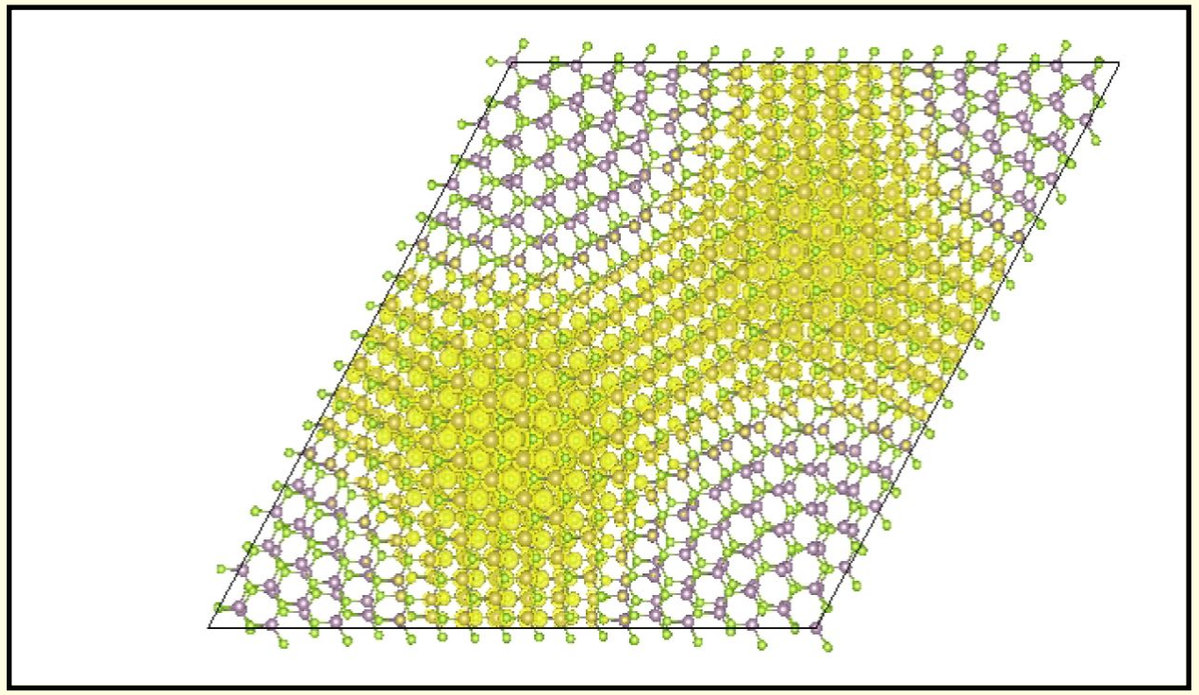


The sub-band formation emerges from concentrated regions of enhanced inter-layer interaction strengths.

At 3.48° with optimised structure.



Shortest set of
Se-Se distances < 3.8 Å



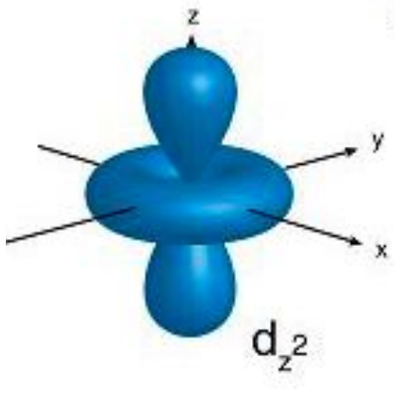
Charge density of the split off band
at Gamma.

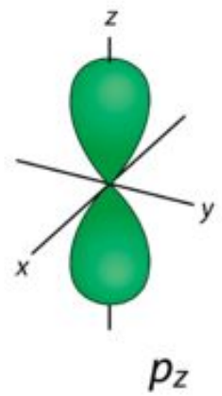
Concentrated regions of enhanced inter-layer interaction strengths lead to sub-band formation for twisted bilayers.

Gamma

$(VBM)_{\Gamma}$ → $d_{z2,}\, p_z$

Out of plane orbitals





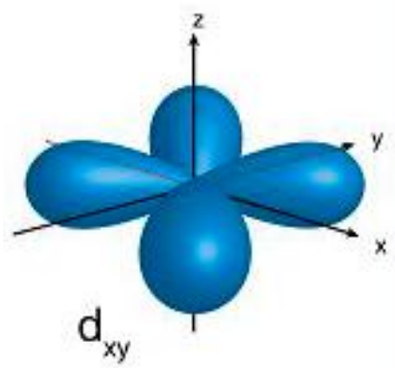
Large Interlayer coupling

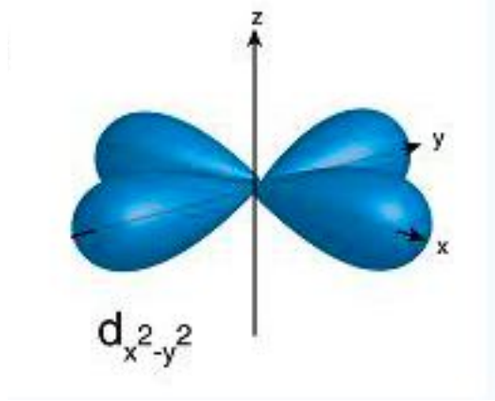
Small Spin orbit coupling

K-valley

$(VBM)_{K}$ → $d_{x2-y2,}\, d_{xy}$

In plane orbitals

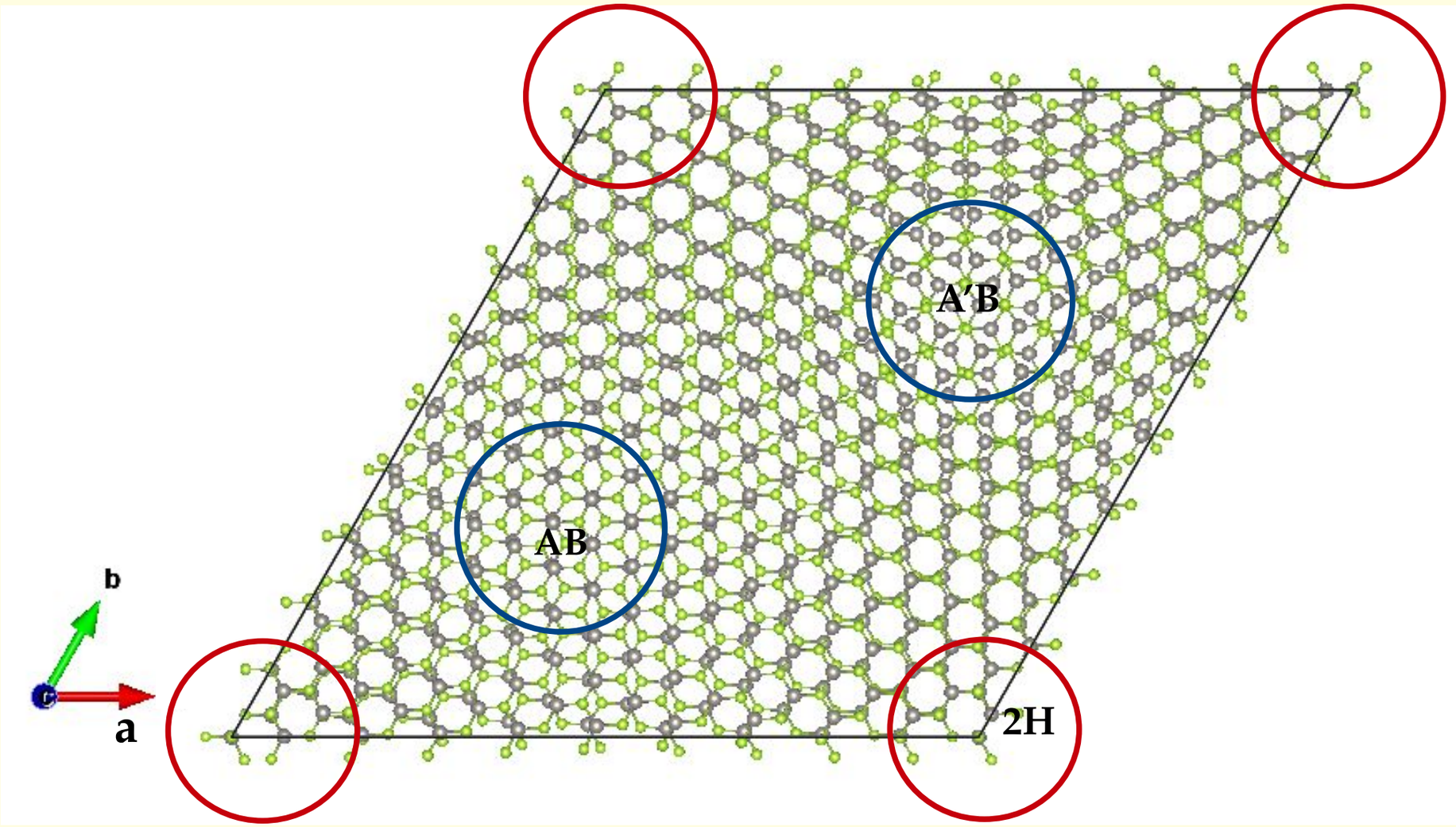




Small Interlayer coupling

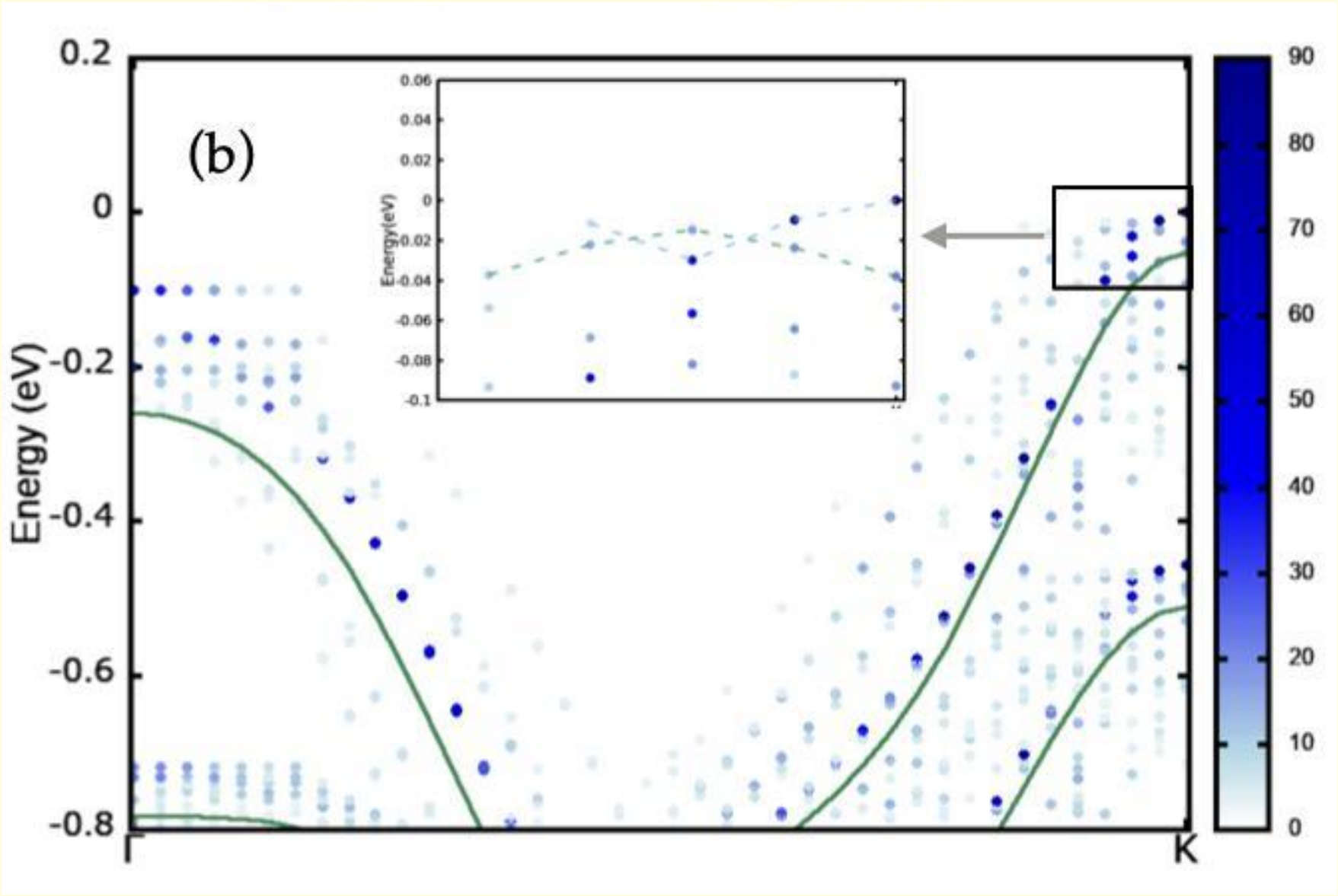
Large Spin orbit coupling

Twisted bilayer WSe_2 at 3.48°

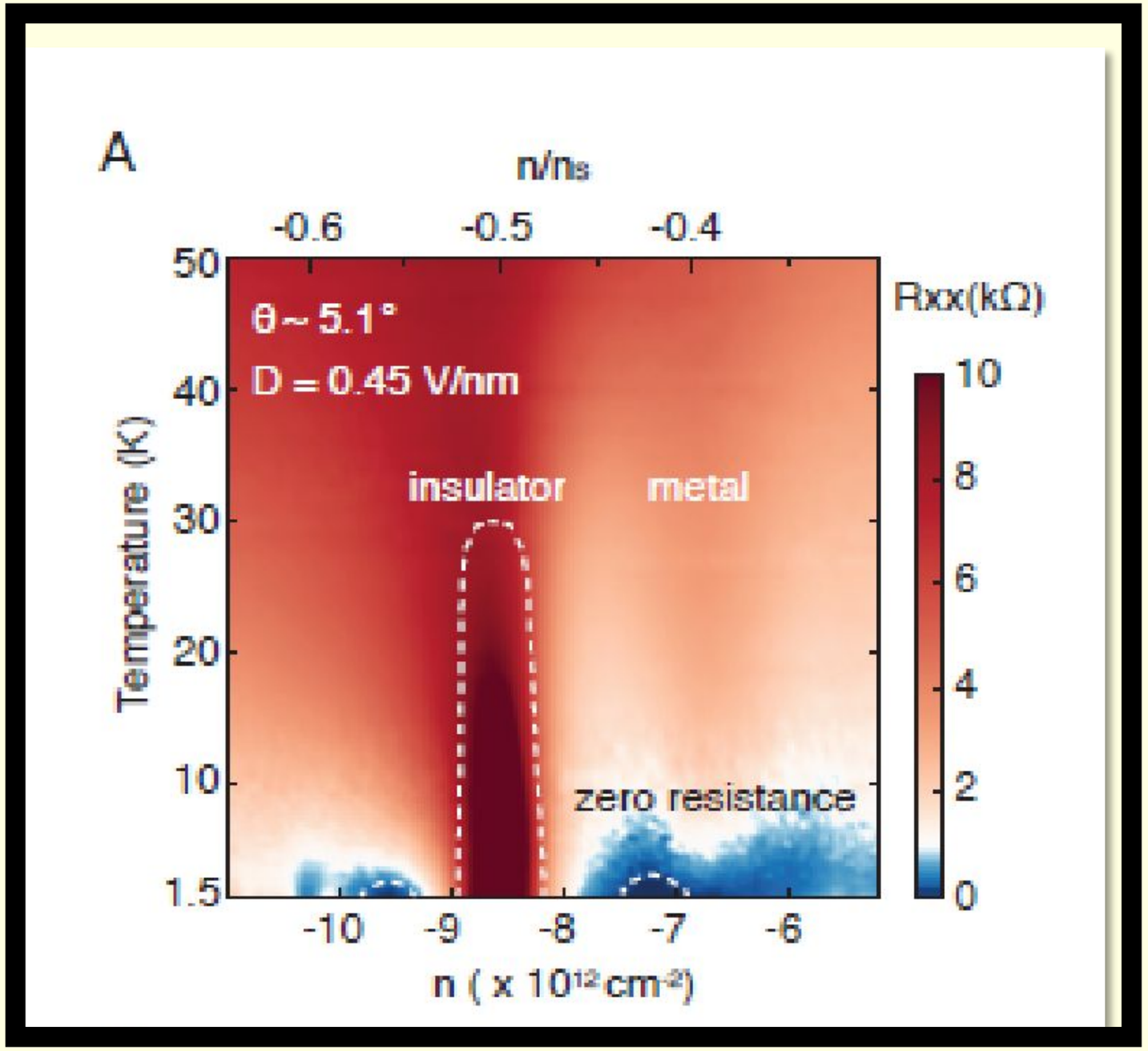


No of atoms=1626 Unit cell dimensions ~ 54.03 A

Twisted bilayer WSe_2 at 3.48°

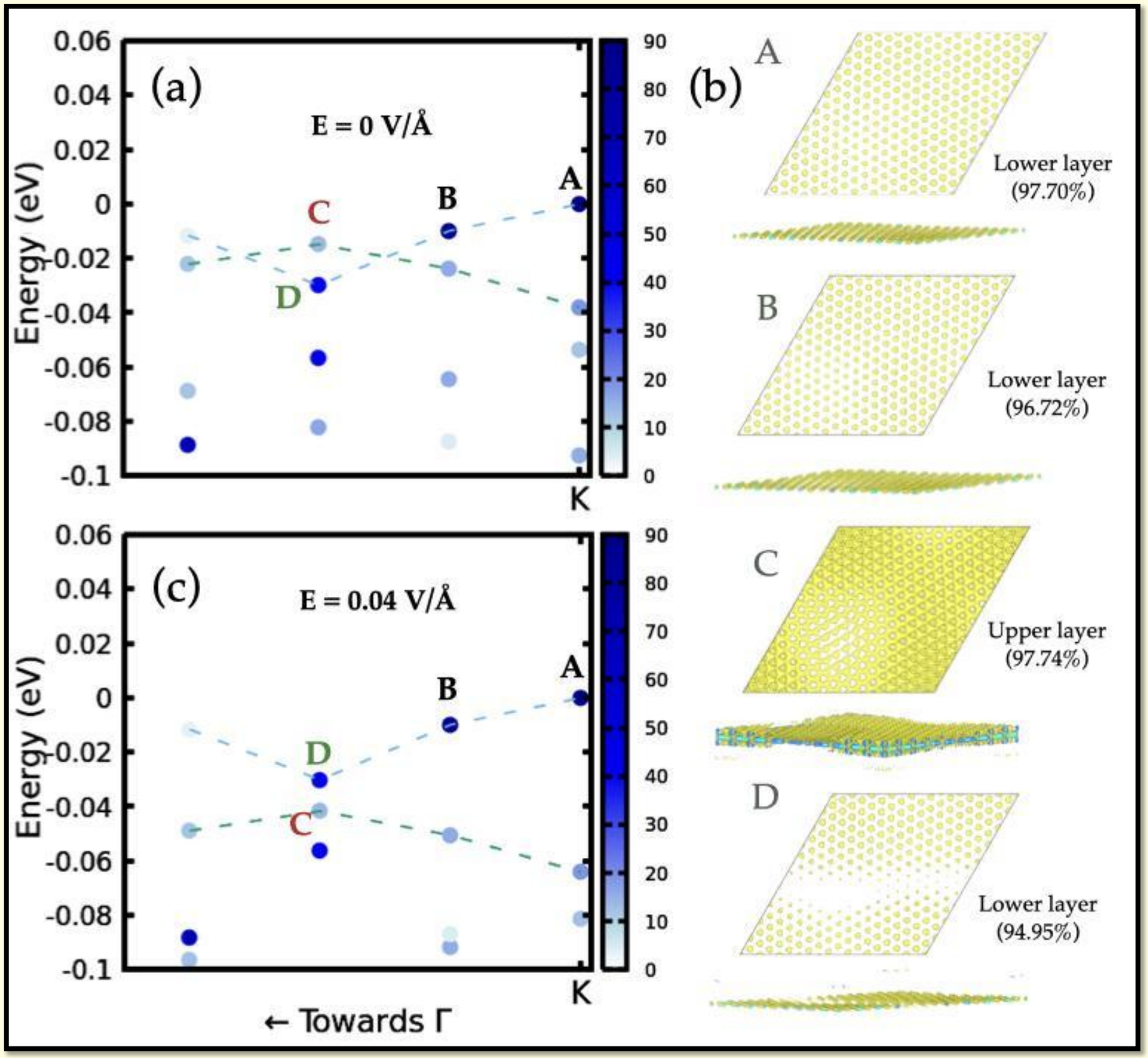


For twisted WSe_2

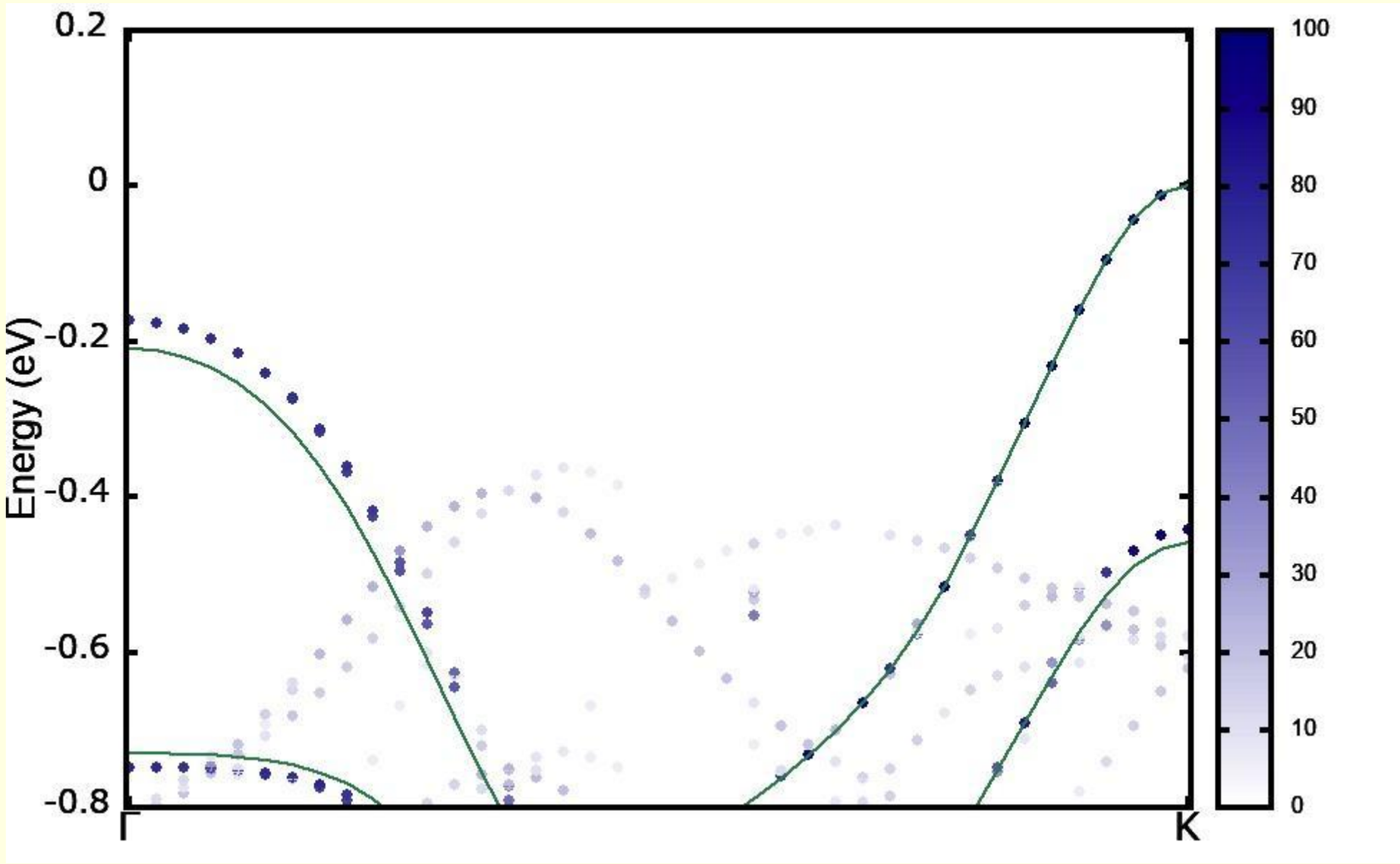


L. Wang et al., Nat. Materials 19, 861 (2020).

Reconstructing the band



Considering a similar sized Moire cell : WSe_2 at 19.03°



Why do we have flat bands at K: what is the perturbation?

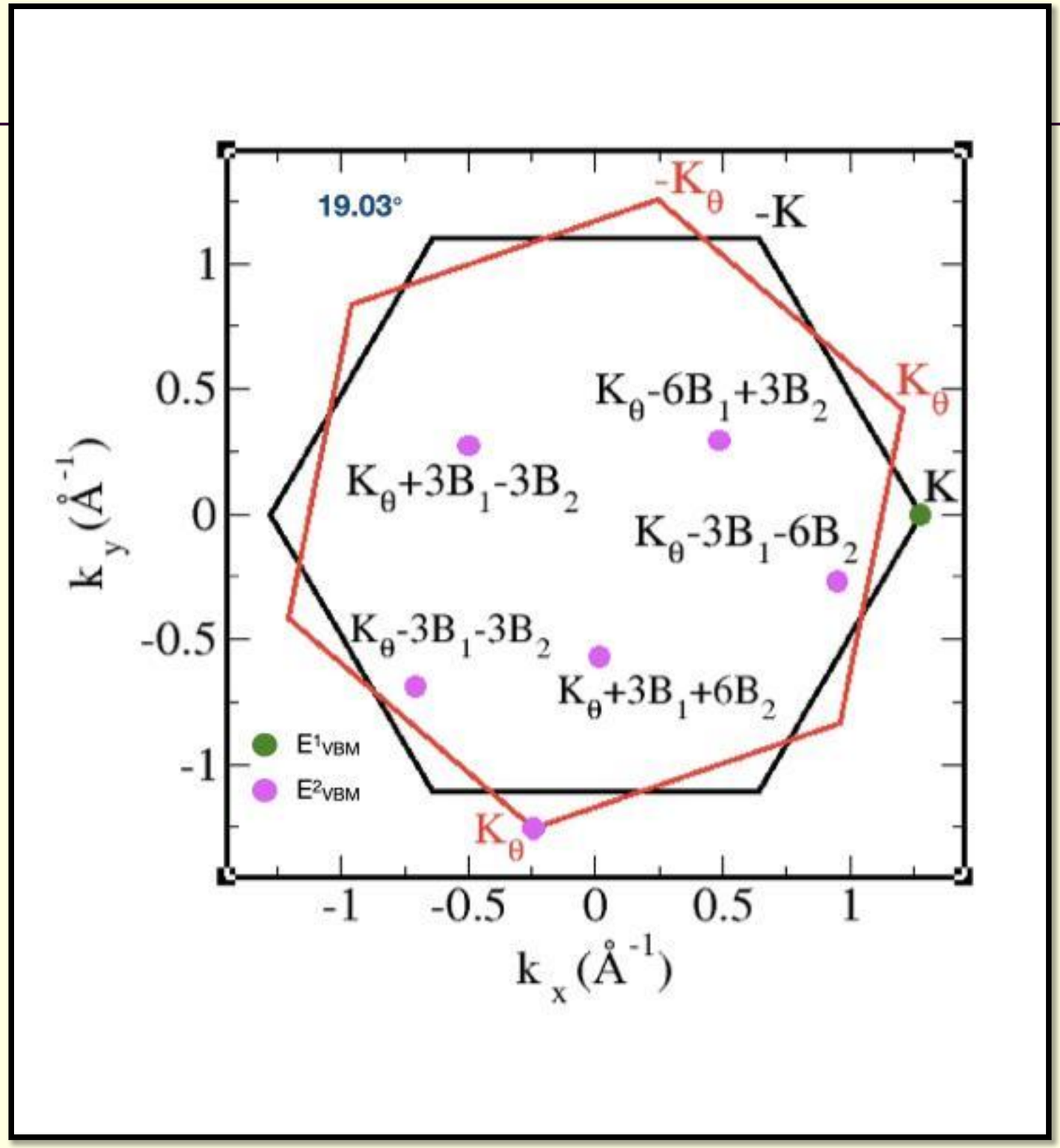
- 3.48° : unit cell length ~54 A°

  19.03° : unit cell length ~ 52 A°

Shouldn't the Moire potentials be similar?

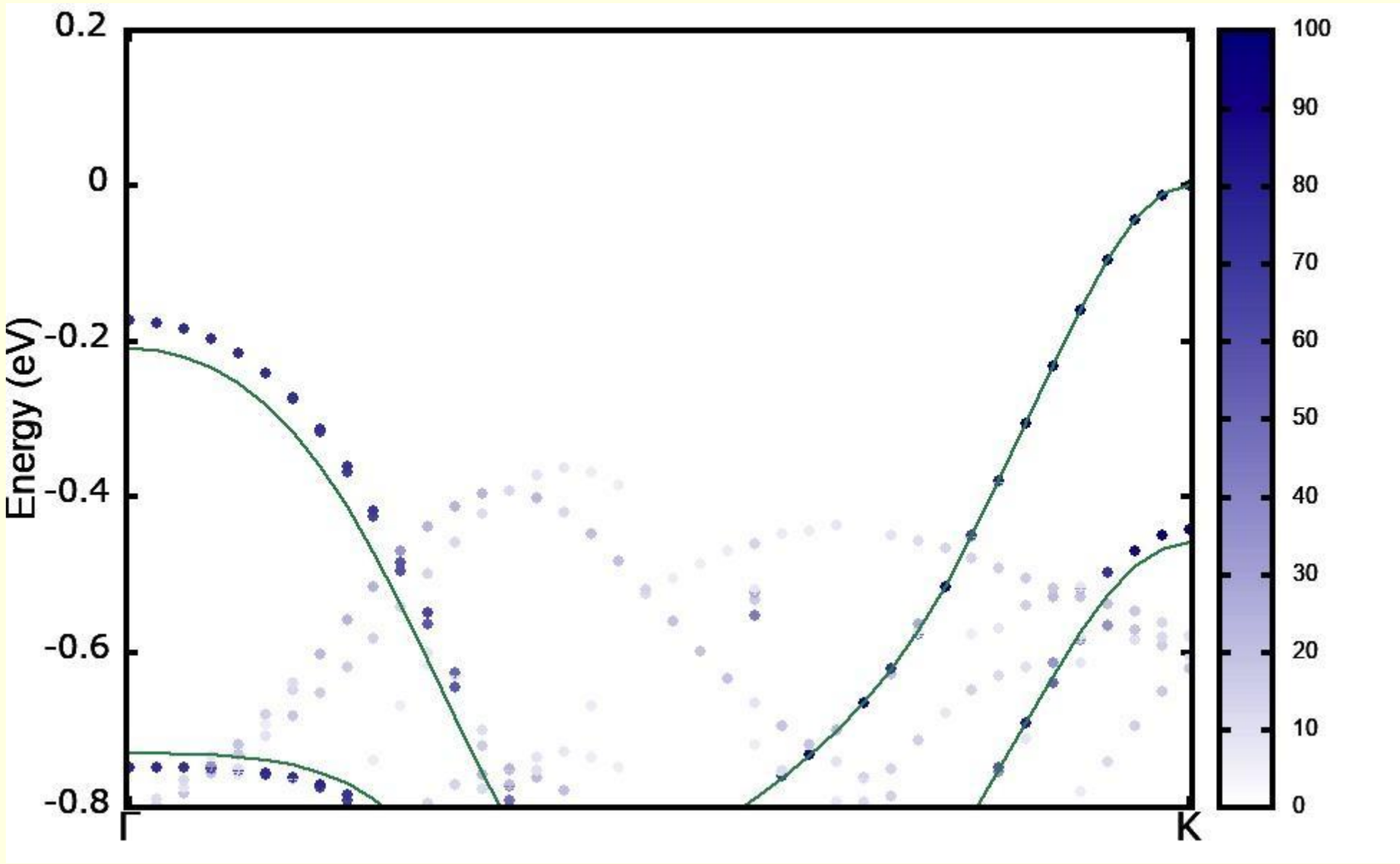
- **Fourier components of the Moire potential are associated with only the reciprocal lattice vectors of the primitive cell.**

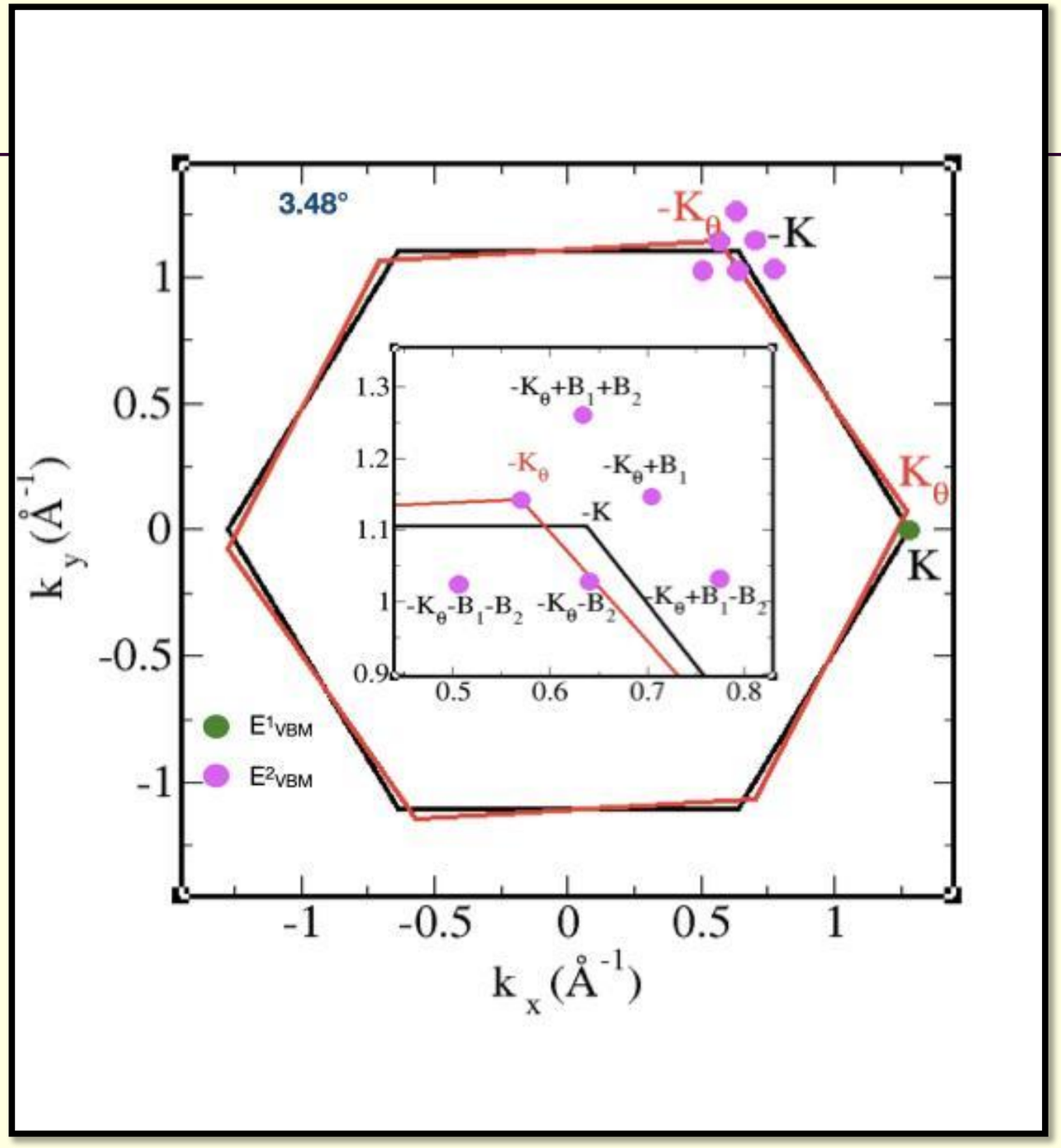
So we need to consider only scattering at the Brillouin zone of the primitive cell.


19.03°
-K$_\theta$
-K
K$_\theta$
K
K$_\theta$-6B$_1$+3B$_2$
K$_\theta$+3B$_1$-3B$_2$
K$_\theta$-3B$_1$-6B$_2$
K$_\theta$-3B$_1$-3B$_2$
K$_\theta$+3B$_1$+6B$_2$
K$_\theta$
E^{1}VBM
E^{2}VBM
1
0.5
0
-0.5
-1
-1
-0.5
0
0.5
1
k$_y$ (Å^{-1})
k$_x$ (Å^{-1})

$$K_{sc} + G = k$$

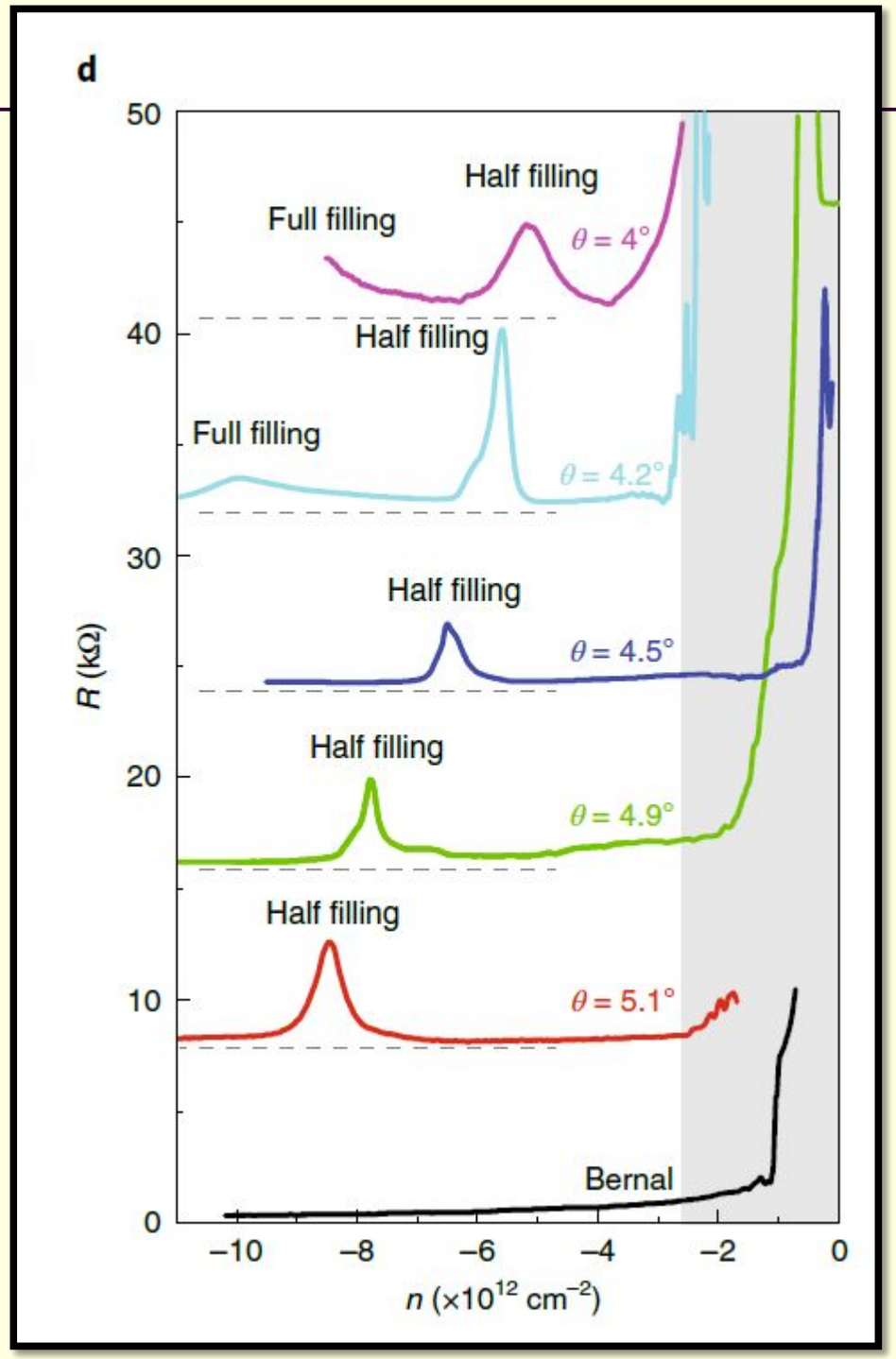
This is why the perturbation is weak at K at 19.03°

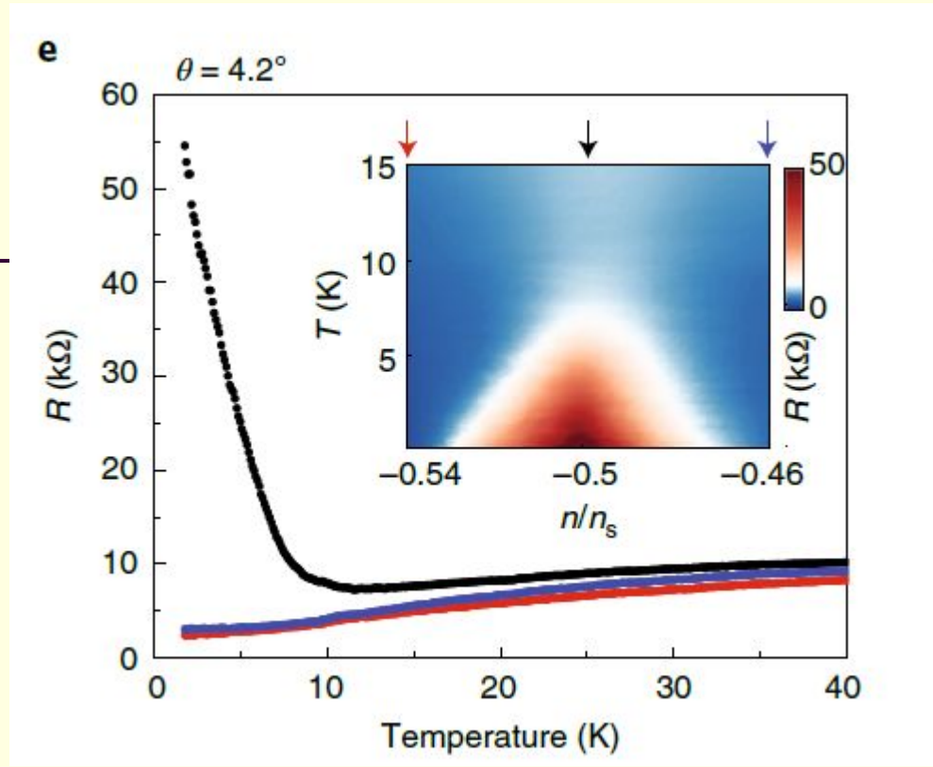



3.48°
-K$_\theta$
-K
K$_\theta$
K
E^1$_{VBM}$
E^2$_{VBM}$
-K$_\theta$+B$_1$+B$_2$
-K$_\theta$
-K$_\theta$+B$_1$
-K
-K$_\theta$-B$_1$-B$_2$
-K$_\theta$-B$_2$
-K$_\theta$+B$_1$-B$_2$
k$_y$ (Å^{-1})
k$_x$ (Å^{-1})

$$K_{sc} + G = k$$

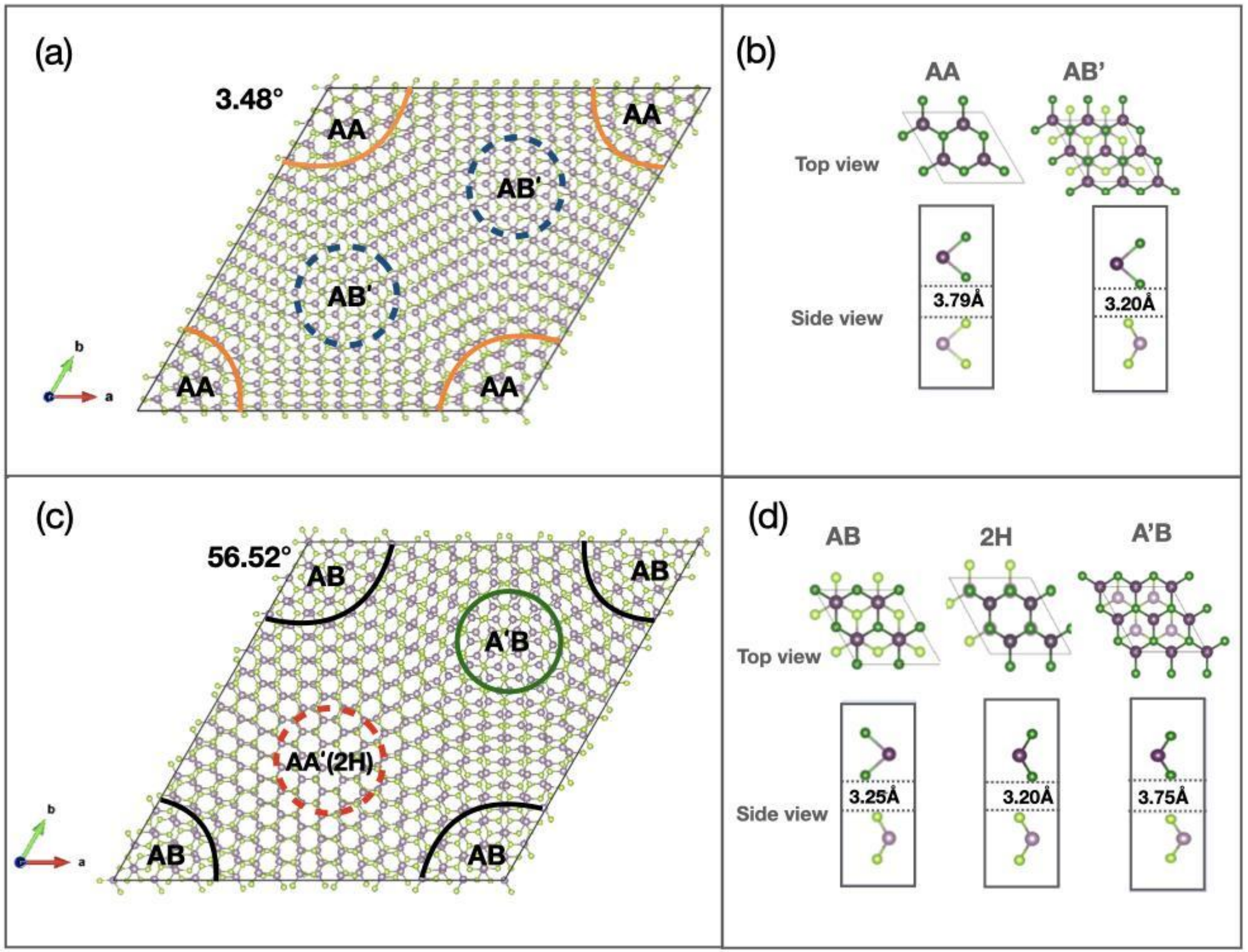
For twisted WSe_2



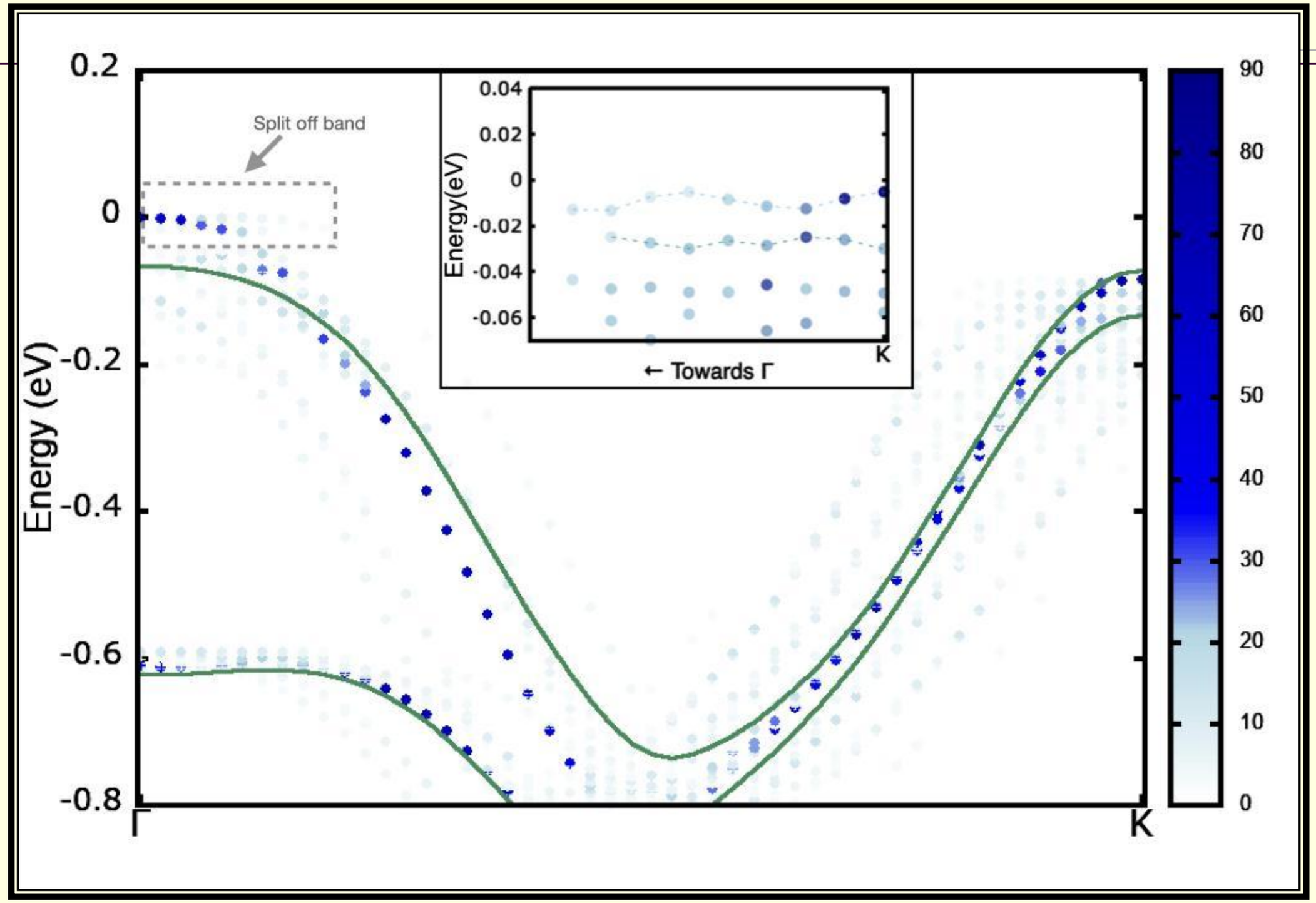


The zone boundary scattering at small angles, reduces the degeneracy of the valence band maximum to 1.

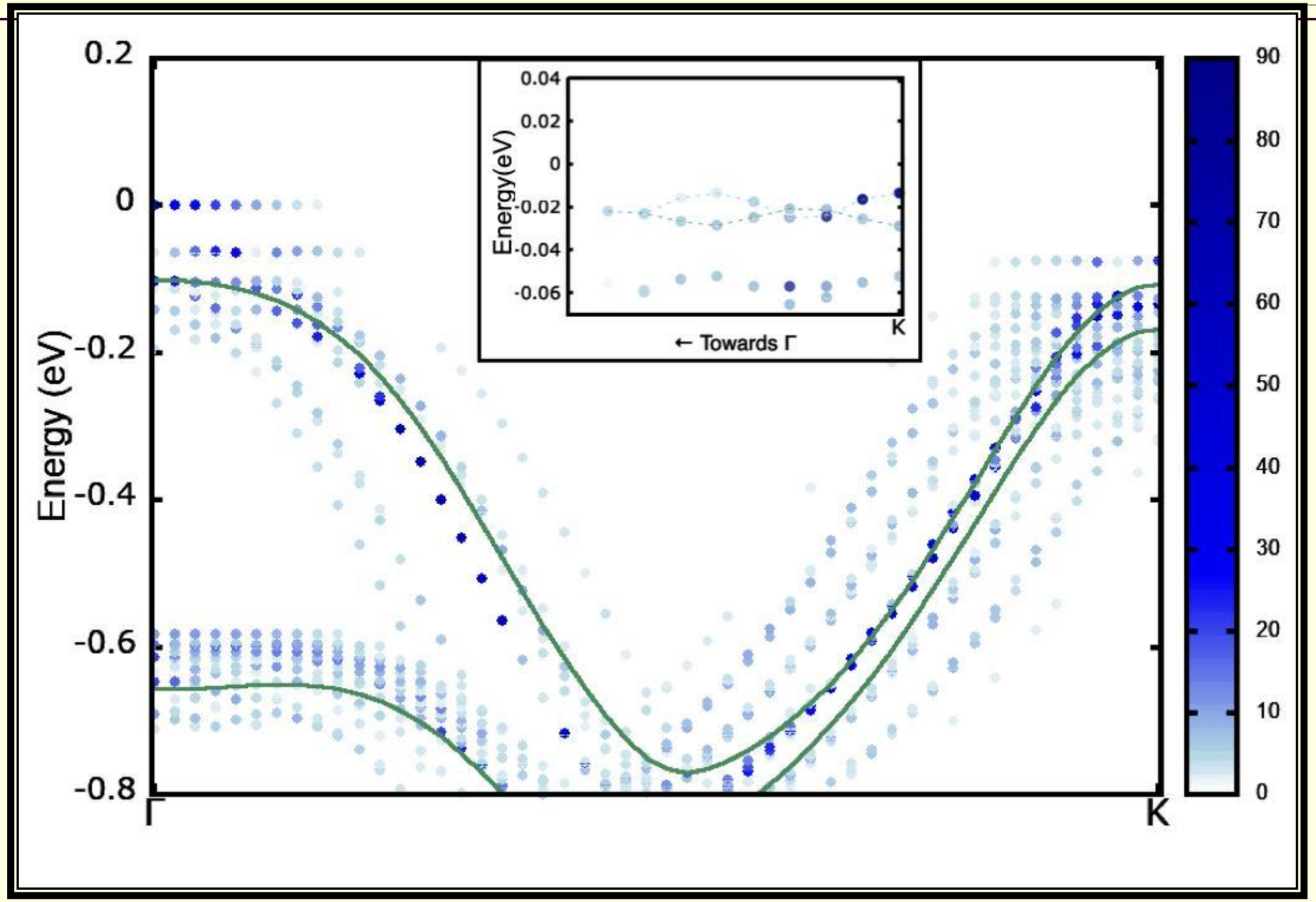
How do we change the number of flat bands?

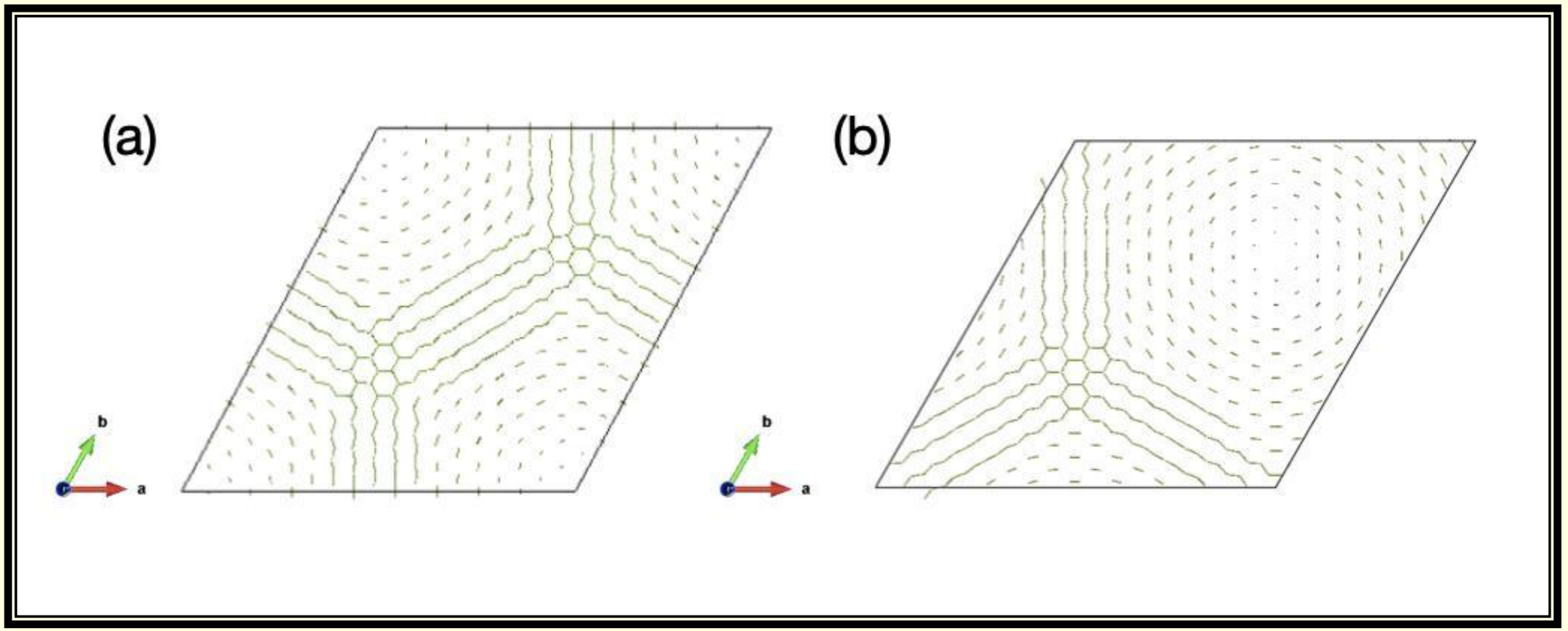

(a)
3.48°
AA
AA
AB'
AB'
AA
AA
b
a
(b)
AA
AB'
Top view
Side view
3.79Å
3.20Å
(c)
56.52°
AB
AB
A'B
AA'(2H)
AB
AB
b
a
(d)
AB
2H
A'B
Top view
Side view
3.25Å
3.20Å
3.75Å

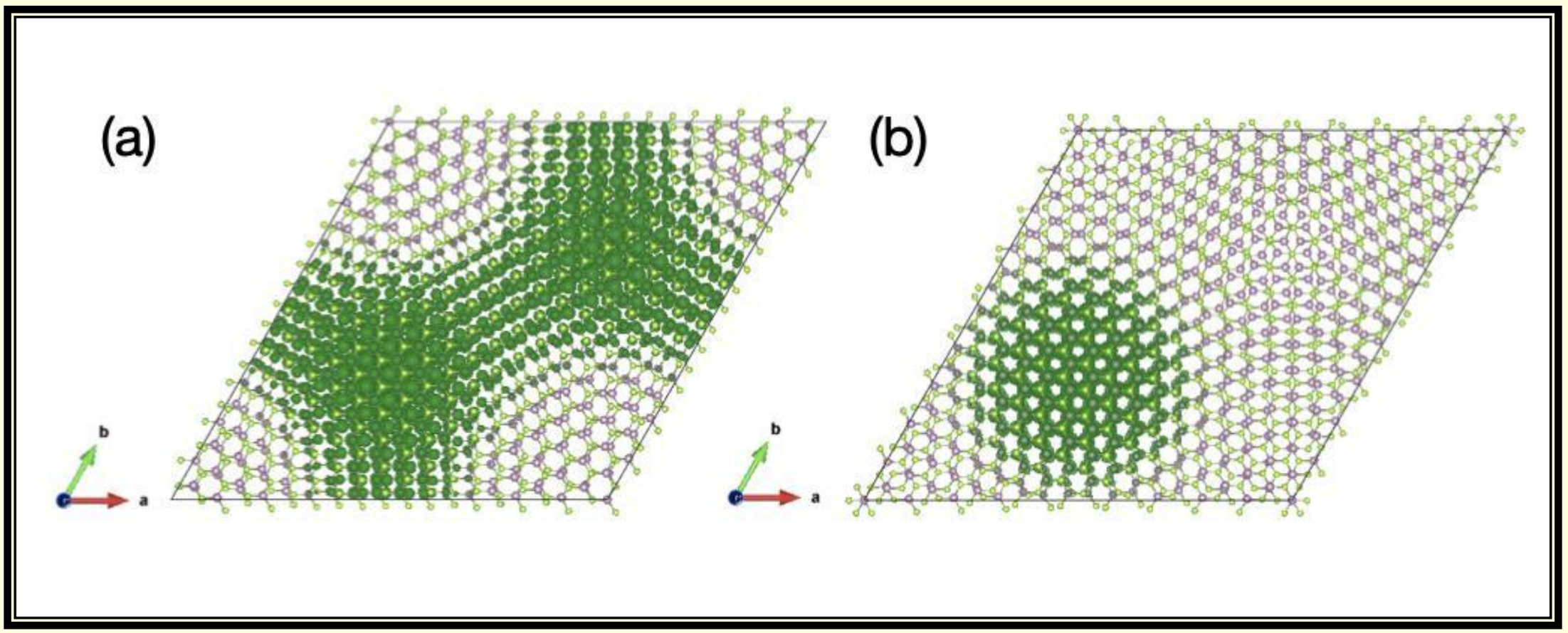
At 3.48°

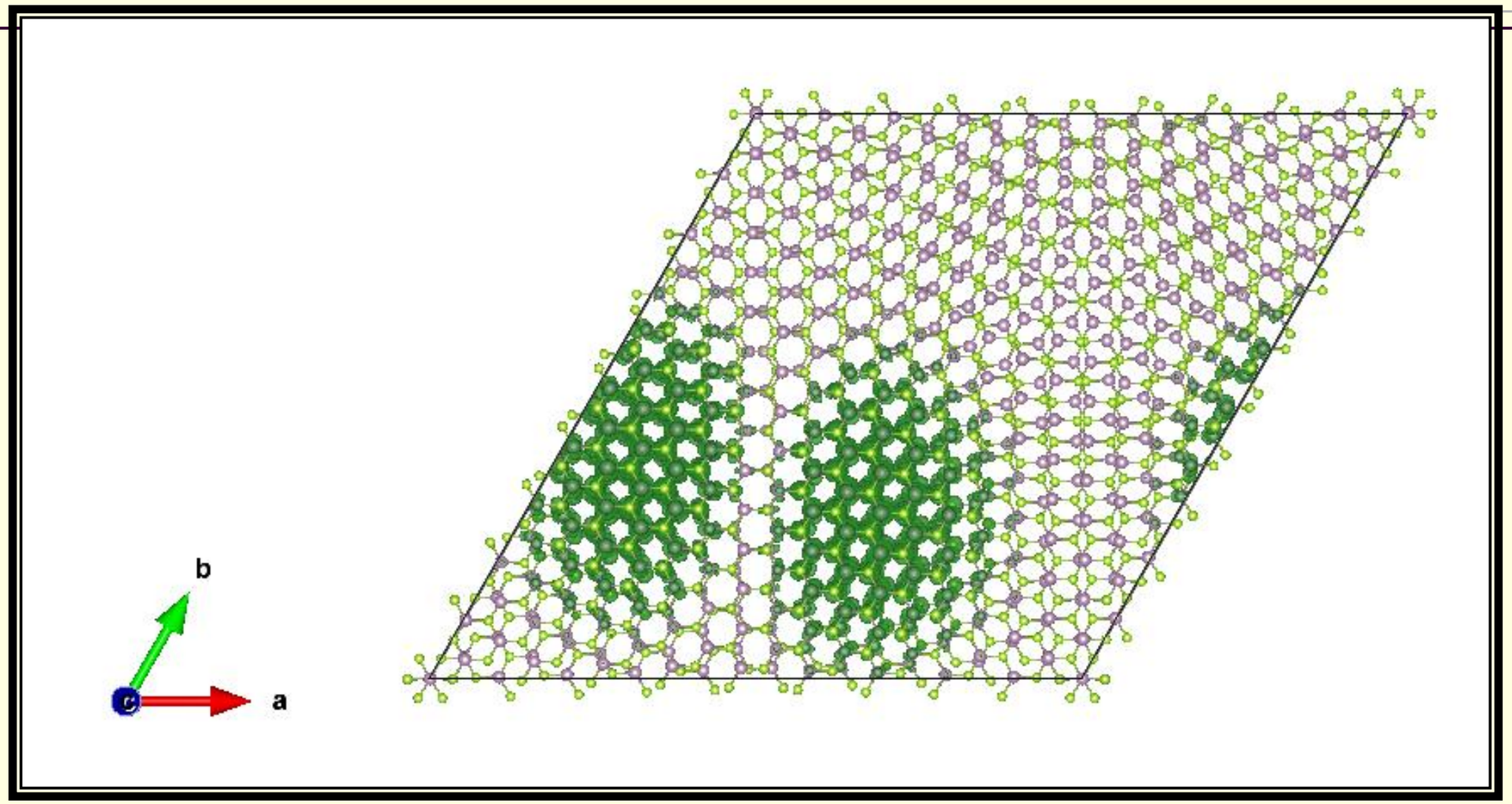

0.2
0
-0.2
-0.4
-0.6
-0.8
Energy (eV)
Split off band
Γ
K
0.04
0.02
0
-0.02
-0.04
-0.06
Energy(eV)
← Towards Γ
K
90
80
70
60
50
40
30
20
10
0

At 56.52°


0.2
0
-0.2
-0.4
-0.6
-0.8
Energy (eV)
Γ
K
0.04
0.02
0
-0.02
-0.04
-0.06
Energy(eV)
← Towards Γ
K
90
80
70
60
50
40
30
20
10
0


(a)
b
a
(b)
b
a


(a)
b
a
(b)
b
a


b
c
a

Concentrated regions of enhanced inter-layer interaction strengths lead to sub-band formation for twisted bilayers of $MoSe_2$.

In WSe_2 we are able to explain the electric field induced MIT. The flat band formation here is traced back to the zone boundary scattering.

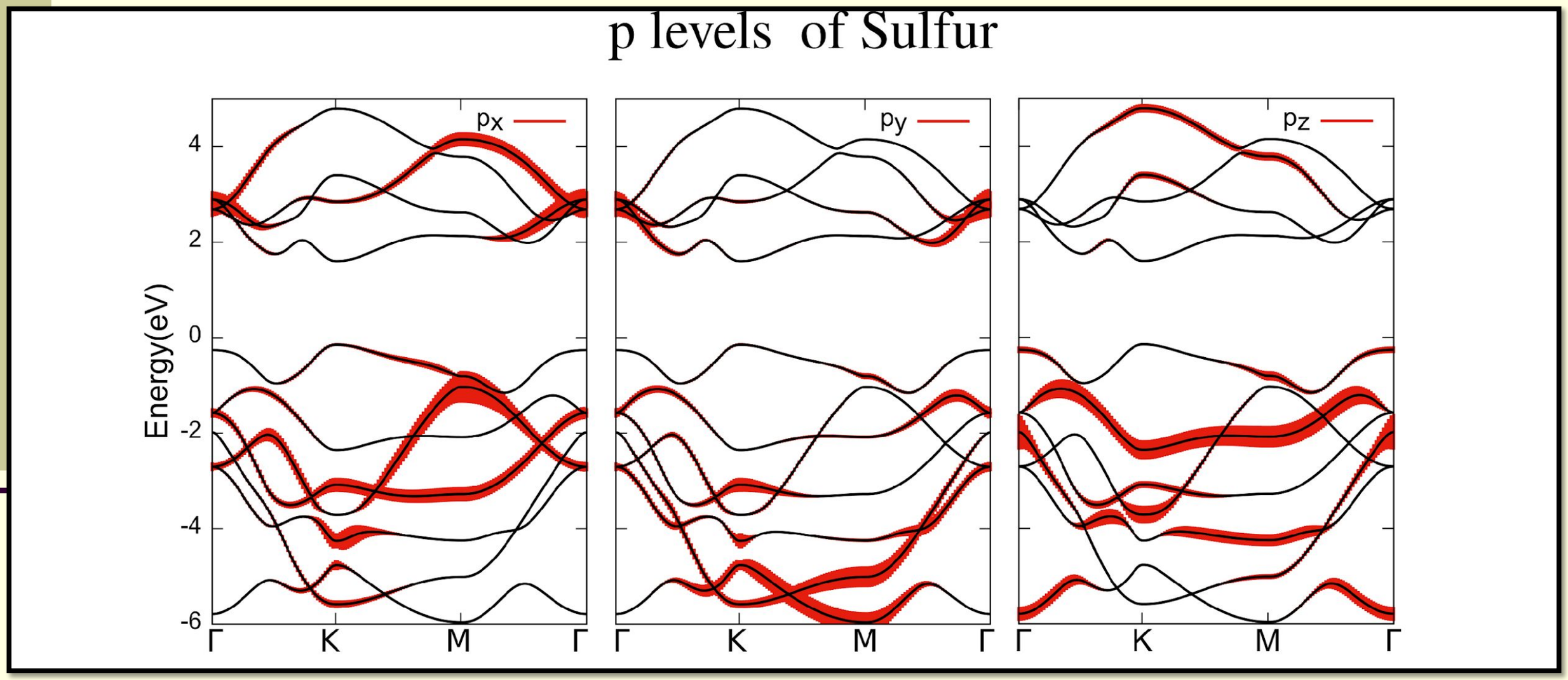
Sumanti Patra

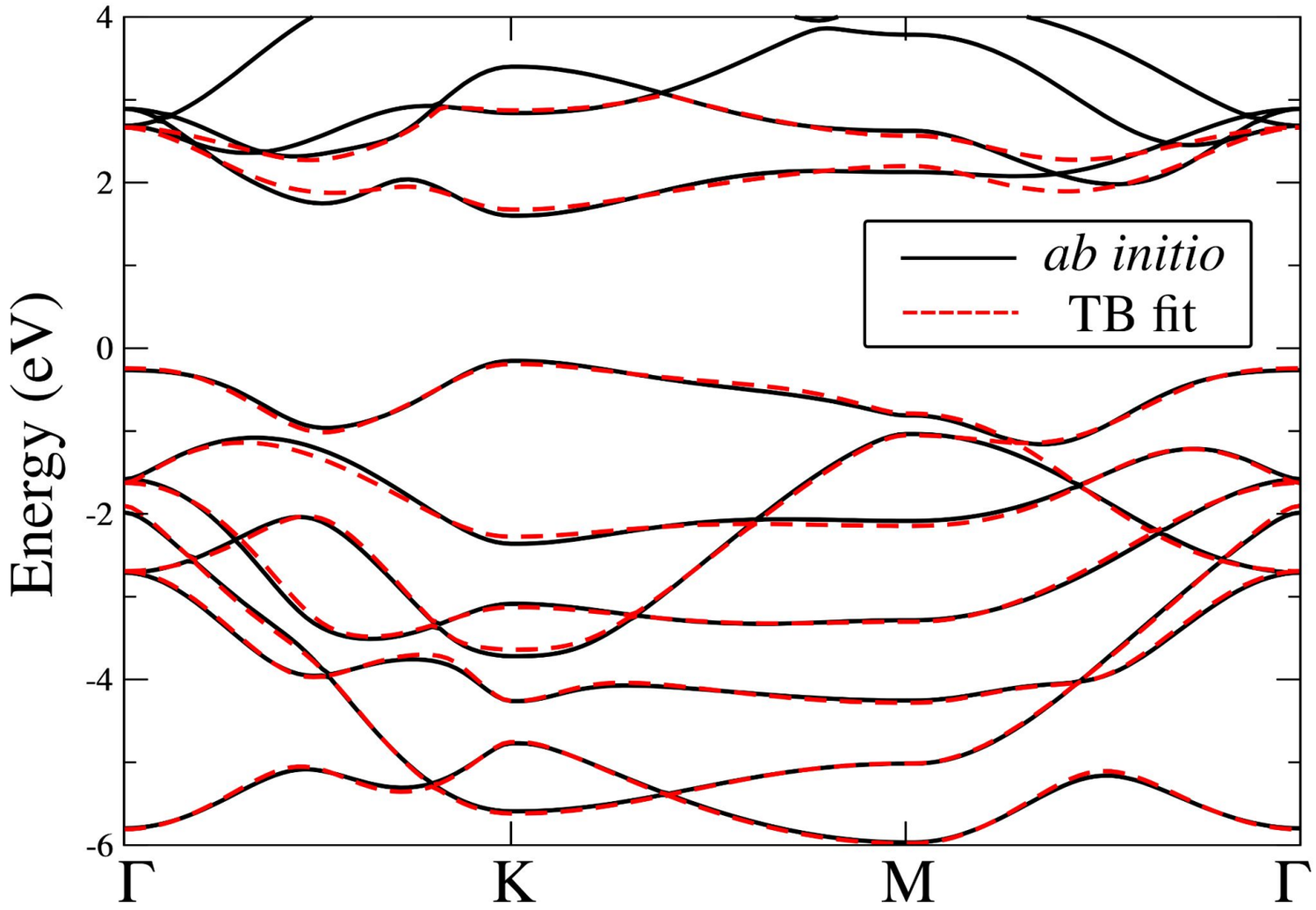
Prasun Boyal

Madhurita Das
Poonam Kumari
Joydeep Chatterjee
Shishir Kumar Pandey
Ruma Das

Sumanti Patra, Poonam Kumari and PM, Phys. Rev. B (2020).
Sumanti Patra, Prasun Boyal and Priya Mahadevan, Phys. Rev. B (Lett.) **107**, L041104 (2023); Sumanti Patra, Madhurita Das and Priya Mahadevan, J. Phys. Mat. **7**, 014001 (2023).
Funding acknowledged from DST Nanomission ; SERB-IRPHA.

Where are the anion p levels?





TB fit with all d and p bands of Mo and S

Effective Hamiltonian at Γ point

-0.21	0.00	0.00
0.00	-0.21	0.00
0.00	0.00	-2.51

Basis : $\{d_{xy}, d_{x2-y2}, d_{z^2}\}$

Effective Hamiltonian at mid-point along Γ-K direction

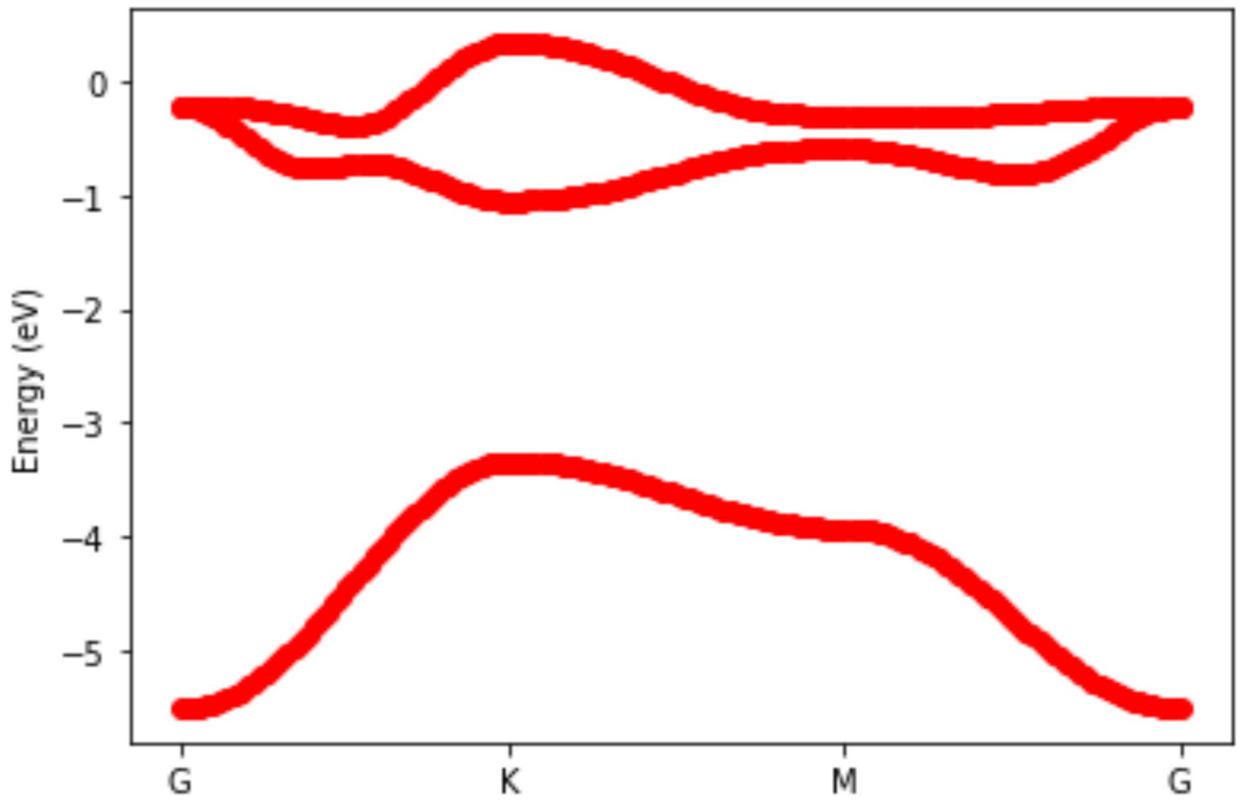
-0.48	0.15-0.03i	-0.22-0.03 i	Basis : {d_{xy} , d_{x2-y2} , d_{z^2}}
0.15+0.03i	-0.65	-0.13+0.04 i	
-0.22+0.03 i	0.13-0.04i	–1.15	

Effective Hamiltonian at K point

$$\begin{pmatrix} -0.35 & -0.69i & 0.00 \\ 0.69i & -0.35 & 0.00 \\ 0.00 & 0.00 & -0.48 \end{pmatrix}$$

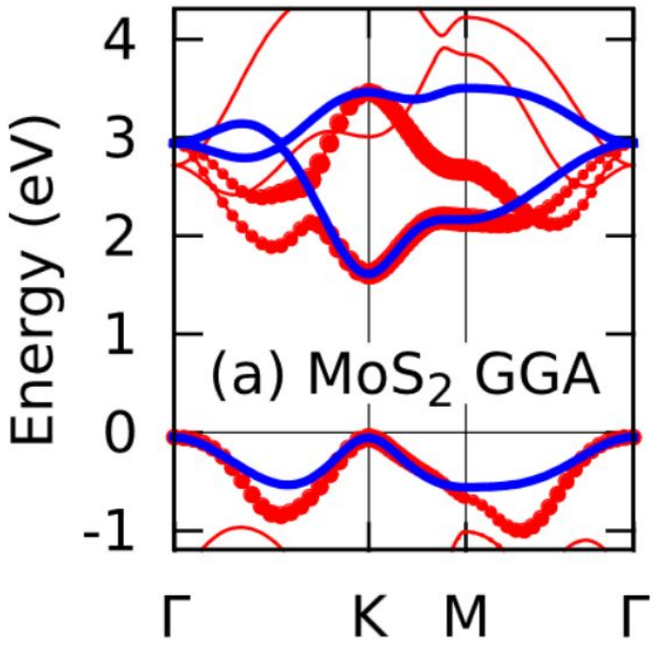
Basis : $\{d_{xy}, d_{x2-y2}, d_{z\hat{}2}\}$

Band structure obtained from
effective *d* only model (downfolded from full Hamiltonian)



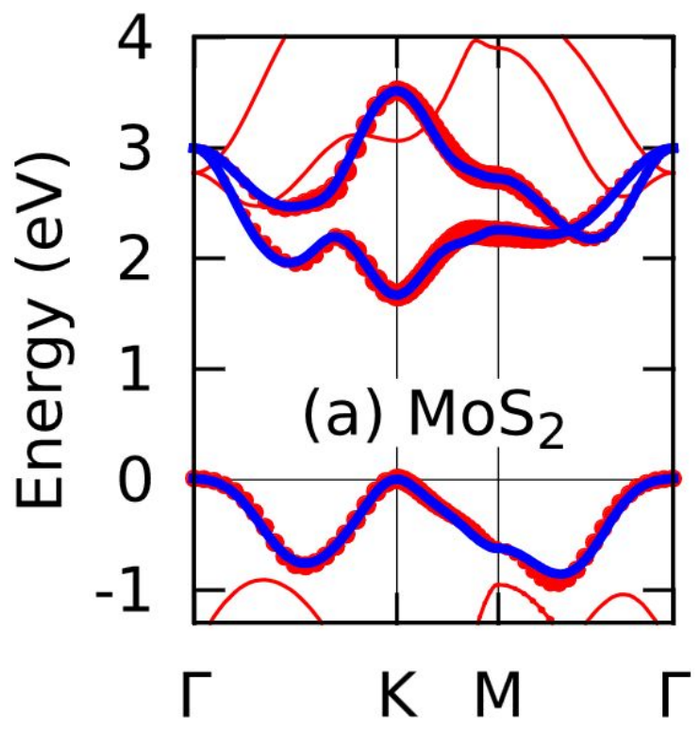
Attempts of d-only model for MoS_2

G. B. Liu et al., PRB **88**, 085433 (2013)

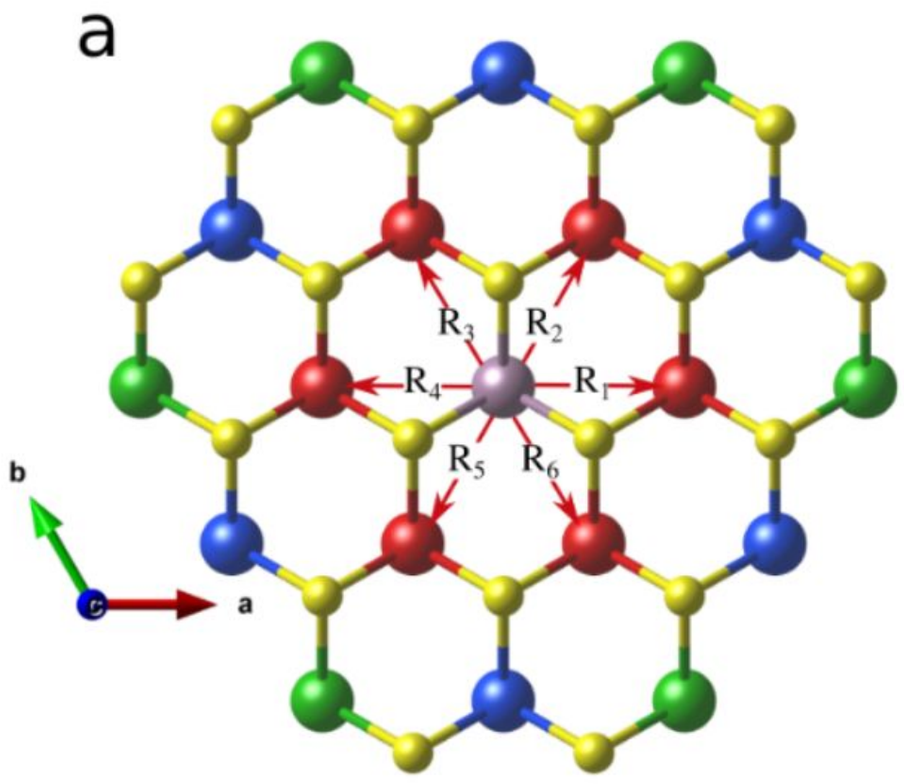


Nearest neighbor model
(8 independent parameter)

Third neighbor model
(17 independent parameter)



Construction of a *d*-only tight binding model



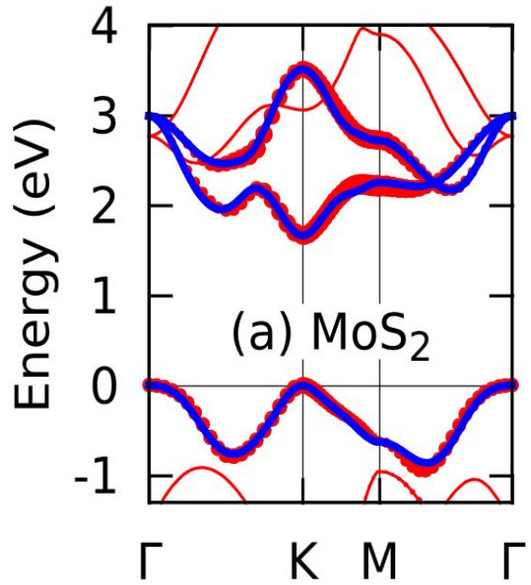
$$\{|1\rangle = |d_{xy}\rangle, |2\rangle = |d_{x^2-y^2}\rangle, |3\rangle = |d_{z^2}\rangle\}$$

Atom number	Lattice vector	Direction cosine (l,m,n)
1	$\boldsymbol{R_1} = \langle a, 0, 0\rangle$	$(1, 0, 0)$
2	$\boldsymbol{R_2} = \langle \frac{a}{2}, \frac{\sqrt{3}a}{2}, 0\rangle$	$(\frac{1}{2}, \frac{\sqrt{3}}{2}, 0)$
3	$\boldsymbol{R_3} = \langle -\frac{a}{2}, \frac{\sqrt{3}a}{2}, 0\rangle$	$(-\frac{1}{2}, \frac{\sqrt{3}}{2}, 0)$
4	$\boldsymbol{R_4} = \langle -a, 0, 0\rangle$	$(-1, 0, 0)$
5	$\boldsymbol{R_5} = \langle -\frac{a}{2}, -\frac{\sqrt{3}a}{2}, 0\rangle$	$(-\frac{1}{2}, -\frac{\sqrt{3}}{2}, 0)$
6	$\boldsymbol{R_6} = \langle \frac{a}{2}, -\frac{\sqrt{3}a}{2}, 0\rangle$	$(\frac{1}{2}, -\frac{\sqrt{3}}{2}, 0)$

$$H_{ij}(\boldsymbol{k}) = \sum_{\boldsymbol{R}} e^{i\boldsymbol{k}\cdot\boldsymbol{R}} E_{ij}(\boldsymbol{R})$$

Where, $E_{ij}(\boldsymbol{R}) = \langle i(\boldsymbol{r})|\hat{H}|j(\boldsymbol{r}-\boldsymbol{R})\rangle$

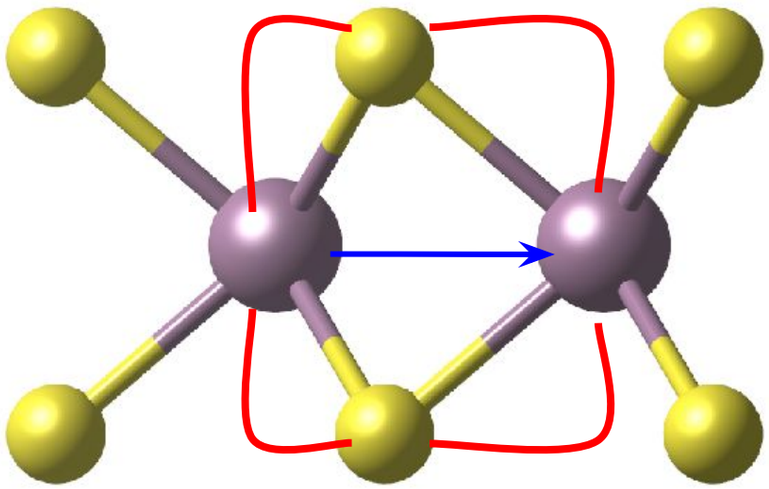
The model fits the bands at the cost of physical meaning!!



G. B. Liu et al., PRB **88**, 085433 (2013)

SK parameter	1^{st} neighbor	2^{nd} neighbor	3^{rd} neighbor
$V_{dd\sigma}$	1.680 ± 0.16	-0.159 ± 0.03	-0.290 ± 0.01
$V_{dd\pi}$	0.085 ± 0.16	-0.040 ± 0.03	0.266 ± 0.01
$V_{dd\delta}$	-1.310 ± 0.16	0.190 ± 0.03	0.147 ± 0.01

Another hopping pathway provided by the S-p states



Two Hopping pathways possible between d states of adjacent Mo atoms!

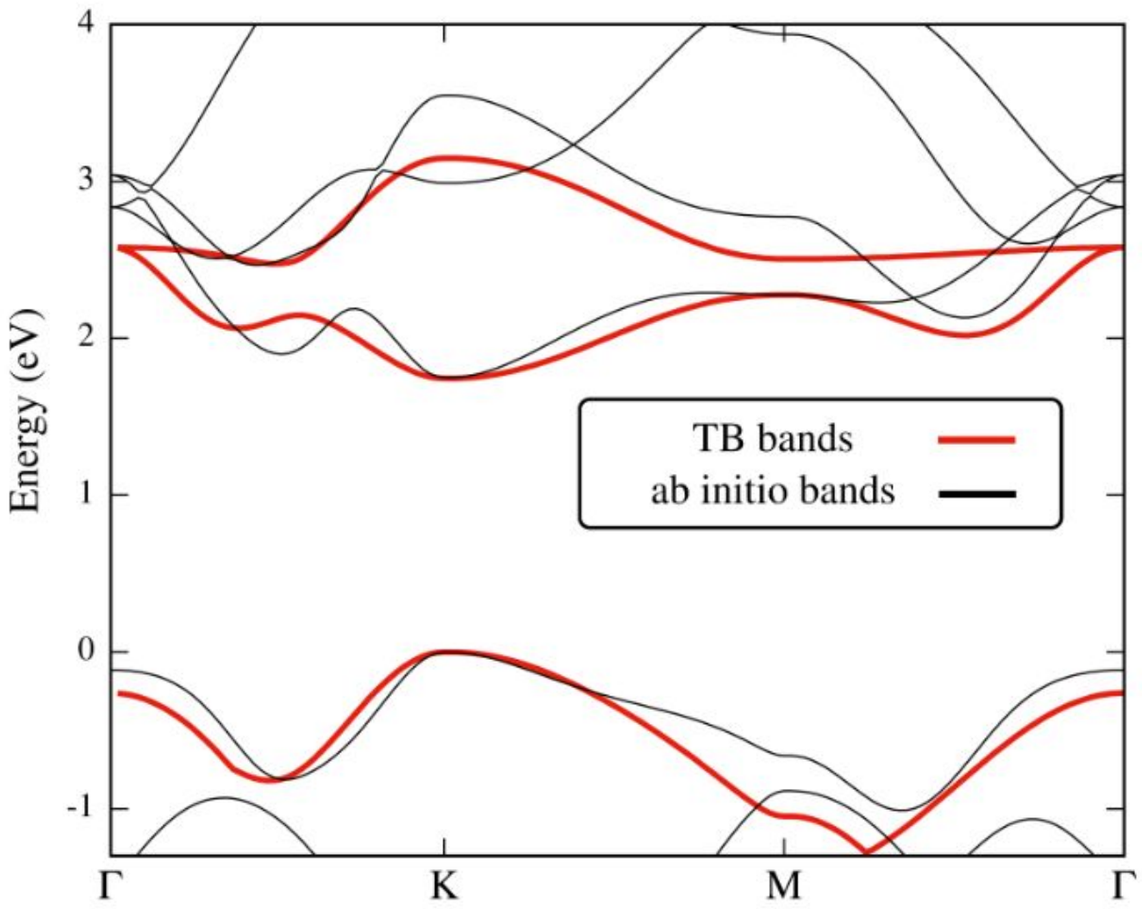
Including in plane p orbitals in the tight binding model

- A 7-band model with in plane *p* orbitals
- Indirect hopping pathways between d electrons via S-p states are also allowed.

Basis: $\{d_{xy}, d_{x^2-y^2}, d_{z^2}, p_x^t, p_y^t, p_x^b, p_y^b\}$

$$\mathcal{H}_{7\text{-band}} = \begin{pmatrix} h_{dd} & h_{dp} \\ h_{dp}^* & h_{pp} \end{pmatrix}$$

Tight binding fit within the 7-band model



ϵ_1	ϵ_2	ϵ_3	$V_{dd\sigma}$	$V_{dd\pi}$	$V_{dd\delta}$	$V_{dp\sigma}$	$V_{dp\pi}$	$V_{pp\sigma}$	$V_{pp\pi}$
-0.84	-4.44	-4.72	-0.04	0.22	-0.19	0.01	-0.58	0.86	-0.03

Effective d-d Hamiltonian

$$\mathcal{H}_{7\text{-band}} = \left(\begin{array}{c|c} h_{dd} & h_{dp} \\ \hline h_{dp}^{*} & h_{pp} \end{array}\right)$$

Effective Downfolded Hamiltonian

$$\mathcal{H}_{eff} = \mathcal{H}_A + \mathcal{V}(\mathbb{I} - \epsilon\mathcal{H}_B)\mathcal{V}^{\dagger}$$

The Effective Hamiltonian

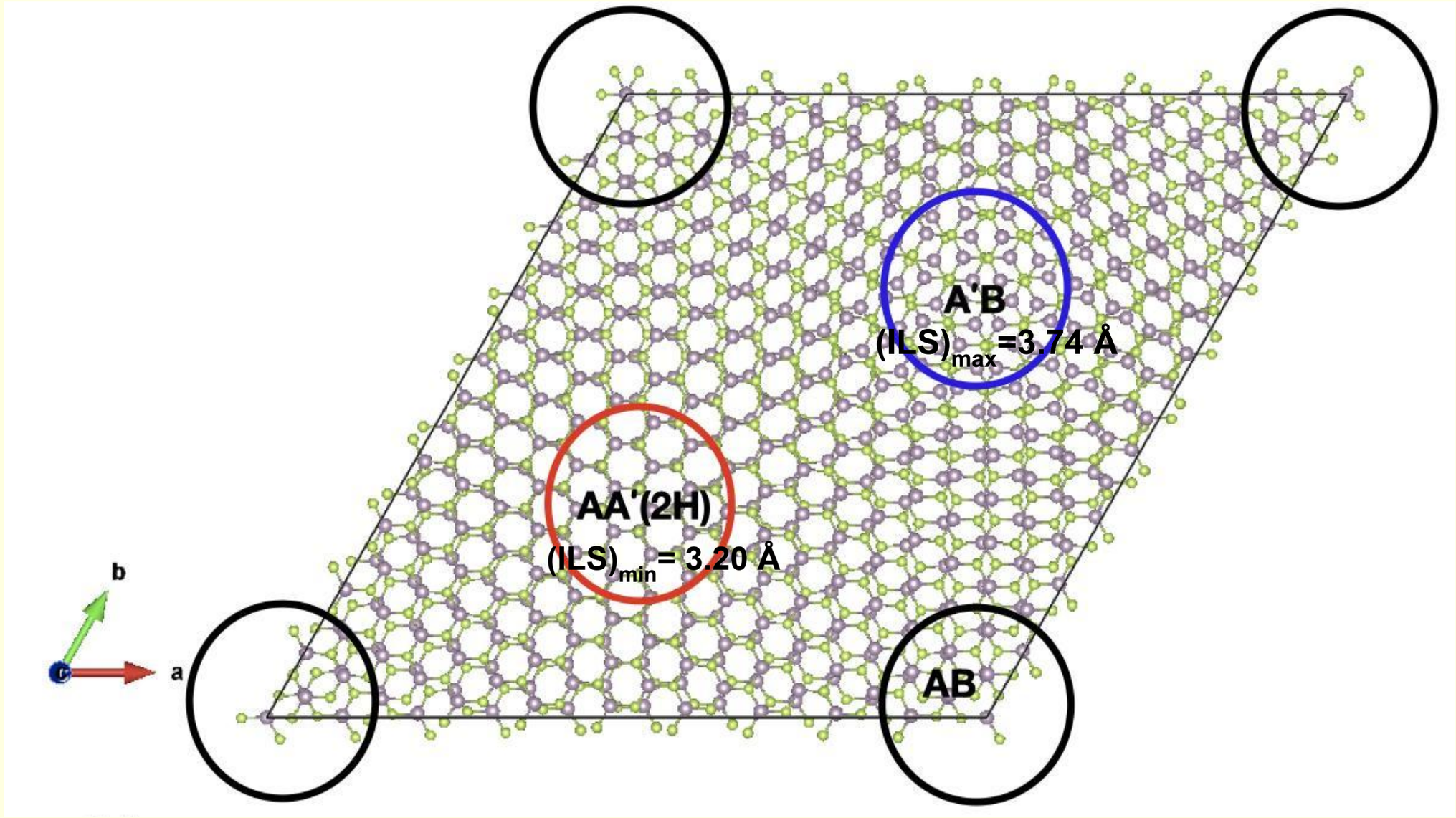
At Γ

$$\begin{pmatrix} -0.4 & 0.00 & 0.00 \\ 0.00 & -0.4 & 0.00 \\ 0.00 & 0.00 & -5.51 \end{pmatrix} \xrightarrow[p \text{ block onto } d \text{ block}]{\text{Downfolding}} \begin{pmatrix} -0.21 & 0.00 & 0.00 \\ 0.00 & -0.21 & 0.00 \\ 0.00 & 0.00 & -5.51 \end{pmatrix}$$

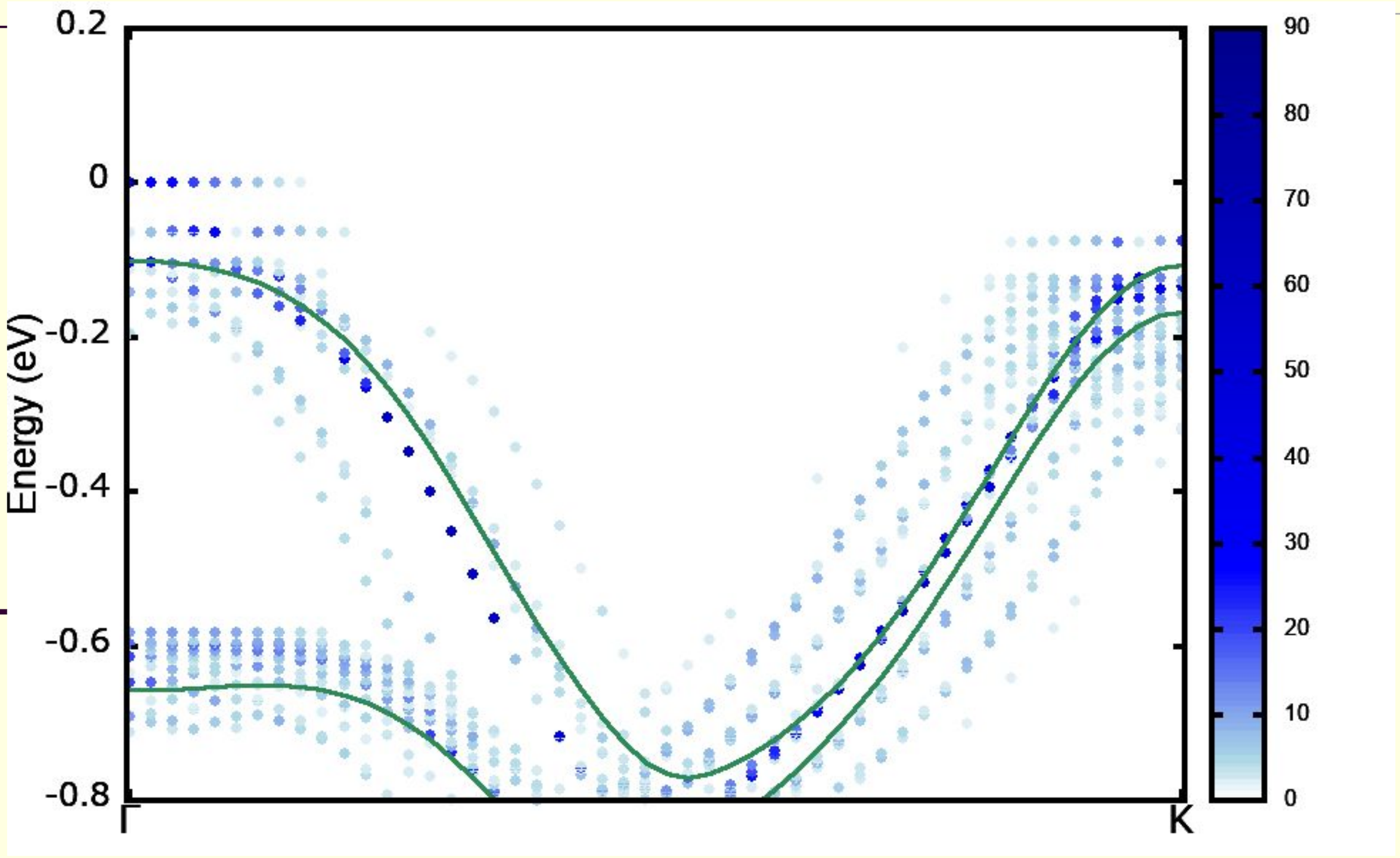
At K

$$\begin{pmatrix} -1.05 & 0.00 & 0.00 \\ 0.00 & -1.05 & 0.00 \\ 0.00 & 0.00 & -3.9 \end{pmatrix} \xrightarrow[p \text{ block onto } d \text{ block}]{\text{Downfolding}} \begin{pmatrix} -0.4 & -0.69i & 0.00 \\ 0.69i & -0.4 & 0.00 \\ 0.00 & 0.00 & -0.5 \end{pmatrix}$$

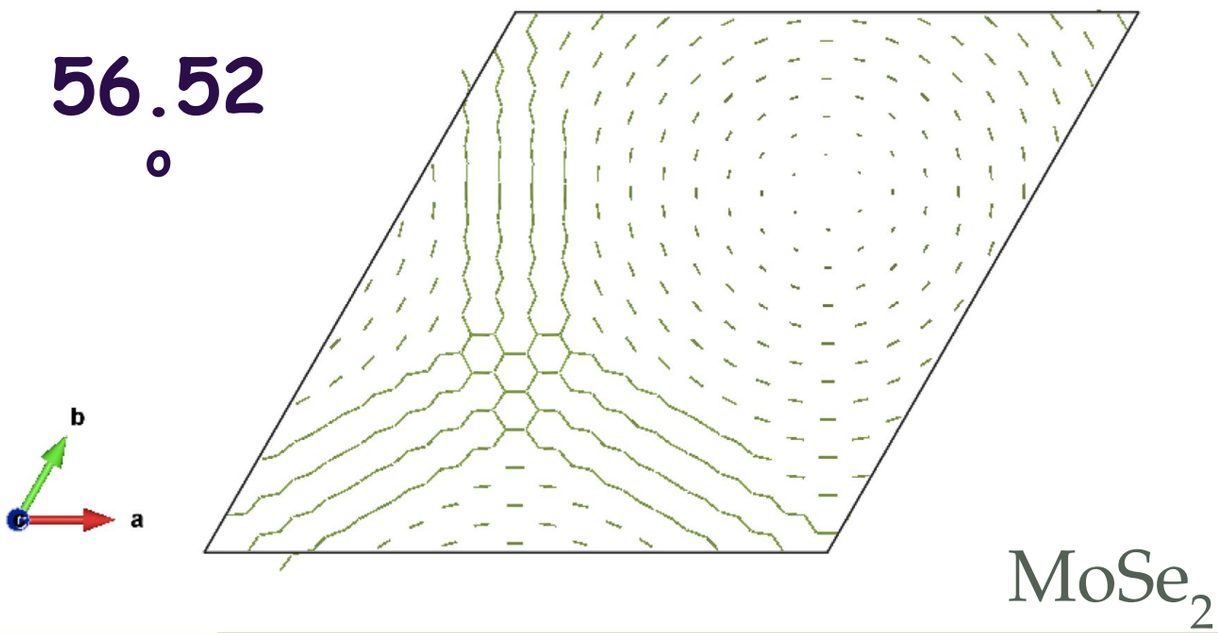
$MoSe_2$ at a twist angle of 56.52°



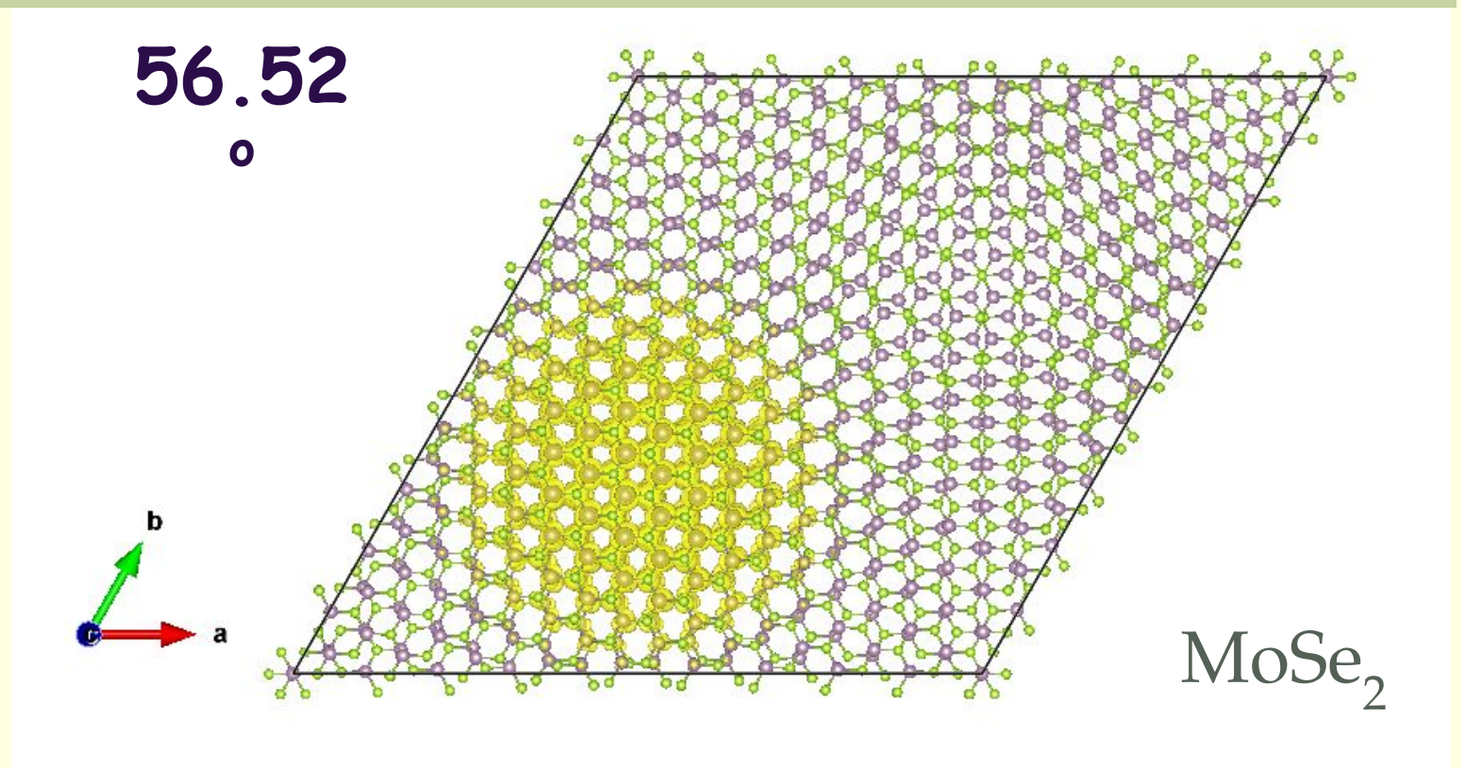
Unfolded band structure (along the primitive cell Gamma to K direction) for twist angle 56.52°



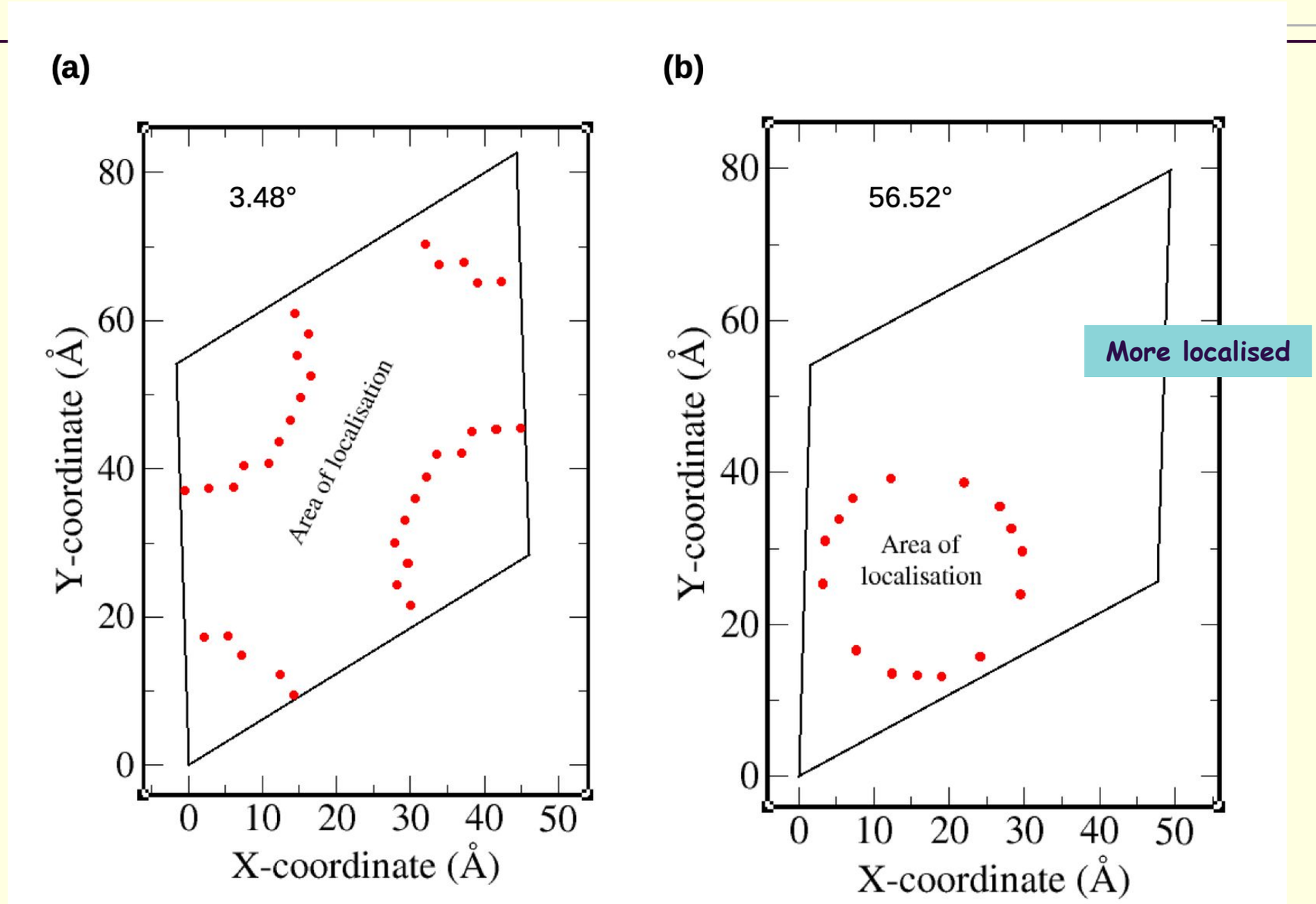
Shortest set of Se-Se distances < 3.8 Å



Charge density of the highest occupied band at Gamma



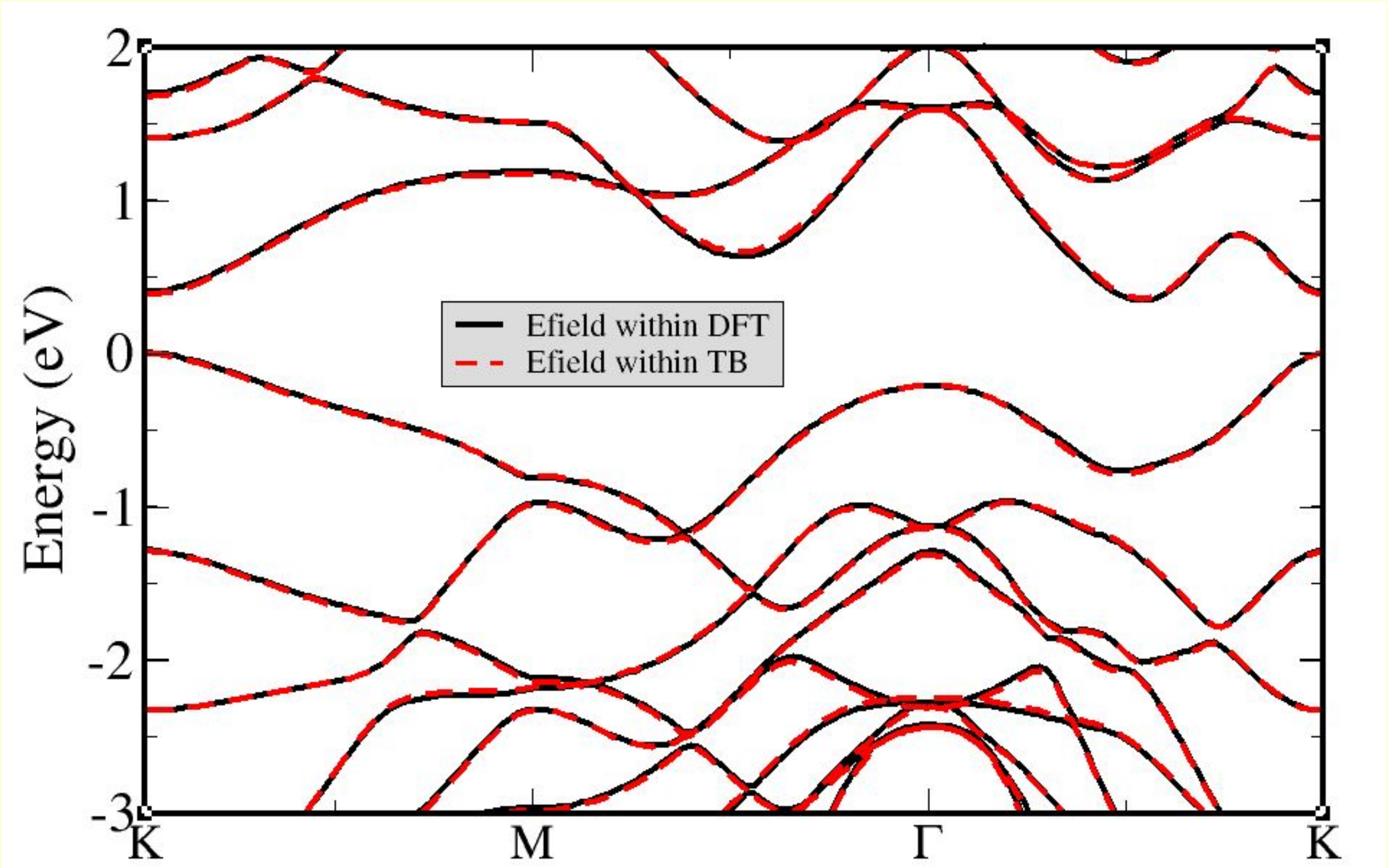
The area of charge density localisation of the split off band up to where the integrated charge density over a sphere of radius 1.262 Å (half the Mo-Se bond length) around each Mo atom reaches 10% of its maximum value.

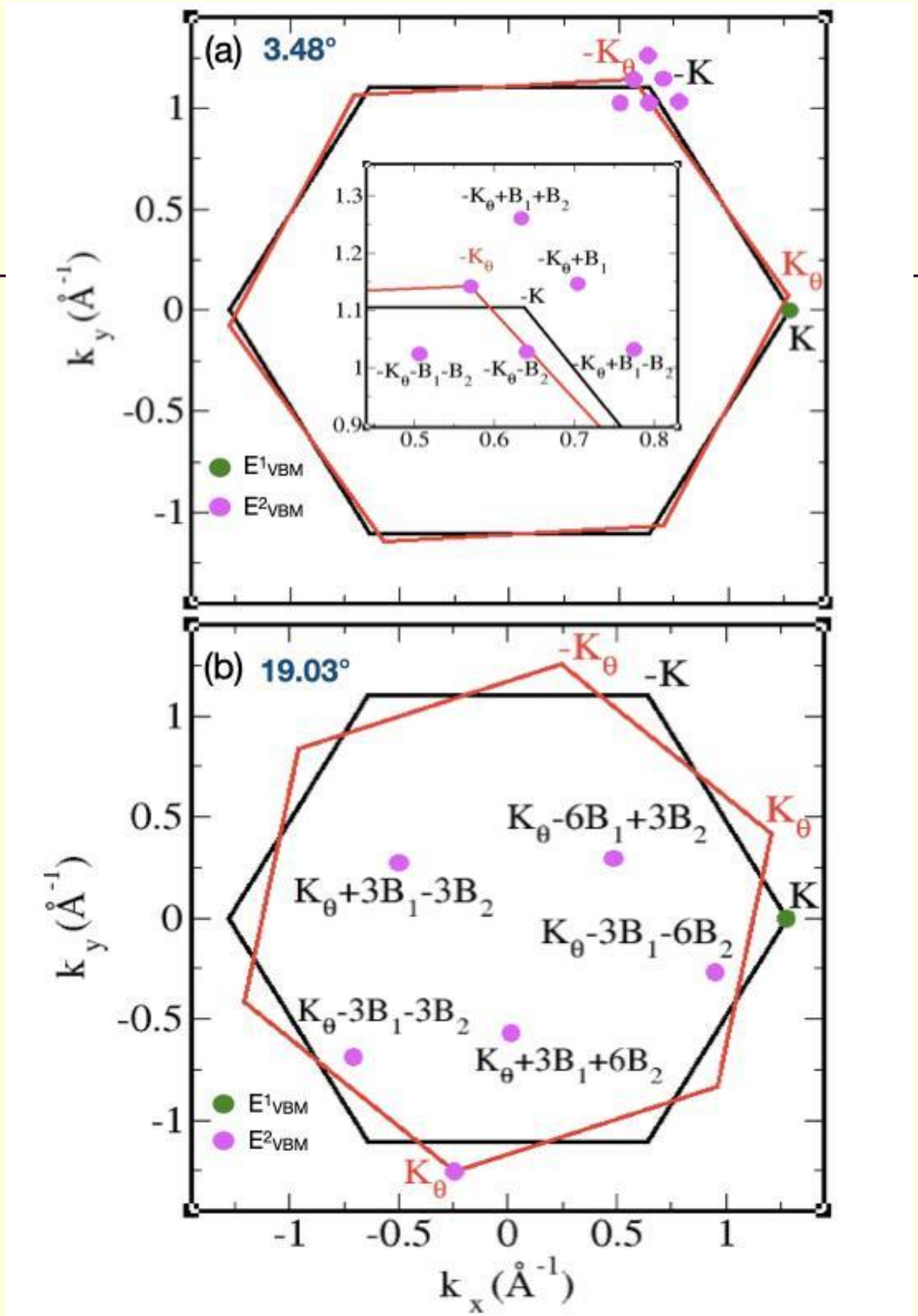


Stronger localisation → Vanishingly small bandwidth

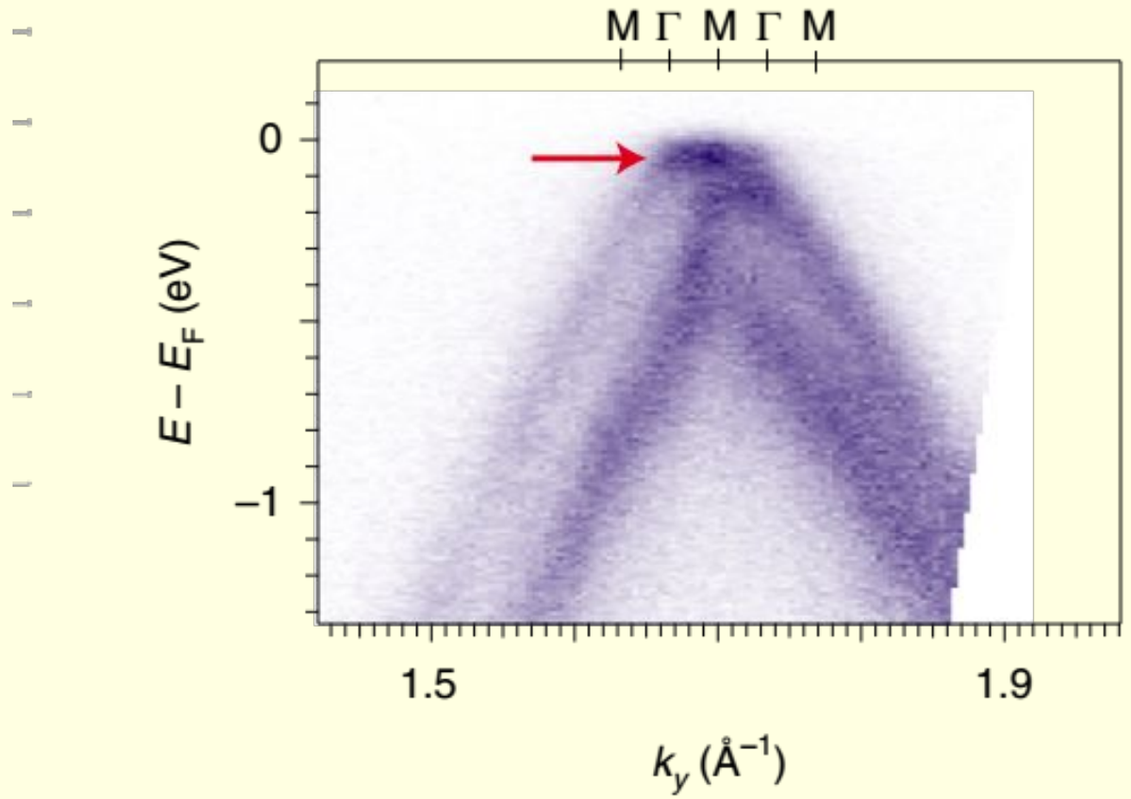
Understanding the effect of vertical electric field on primitive cell bilayer WSe_2

E.z term added to the onsite energies.




(a) 3.48°
-K$_\theta$
-K
K$_\theta$
K
-K$_\theta$+B$_1$+B$_2$
-K$_\theta$
-K$_\theta$+B$_1$
-K
-K$_\theta$-B$_1$-B$_2$
-K$_\theta$-B$_2$
-K$_\theta$+B$_1$-B$_2$
E^{1}VBM
E^{2}VBM
k$_y$ (Å^{-1})
(b) 19.03°
-K$_\theta$
-K
K$_\theta$
K
K$_\theta$-6B$_1$+3B$_2$
K$_\theta$+3B$_1$-3B$_2$
K$_\theta$-3B$_1$-6B$_2$
K$_\theta$-3B$_1$-3B$_2$
K$_\theta$+3B$_1$+6B$_2$
K$_\theta$
E^{1}VBM
E^{2}VBM
k$_y$ (Å^{-1})
k$_x$ (Å^{-1})

K + G = k



Simone Lisi et al., Nat. Phys. 17, 189 (2021).

Recent results in twisted bilayer graphene support this viewpoint.