Class 11
Van der Waals Materials

28.04.2025

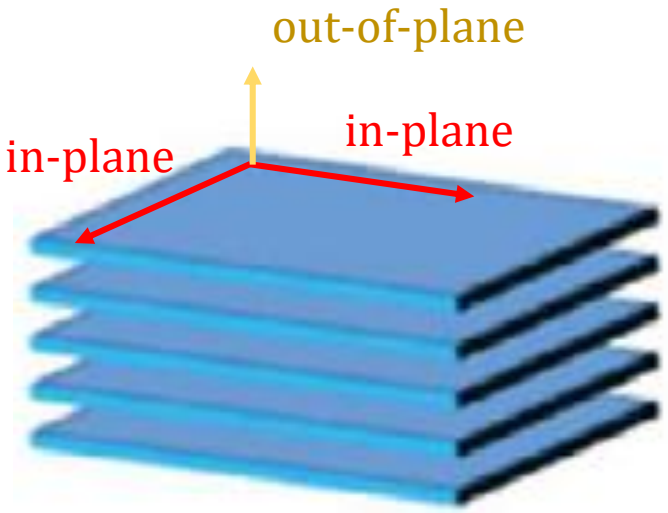
- ❑ Layered crystals
  - Crystal structure
  - Layer dependent band structure
  - Spin-valley locking
- ❑ Effect of stacking order
  - Parallel configuration
  - Antiparallel configuration
  - Twisted layers
- ❑ Doping strategies

VdW Materials = 2D Crystals

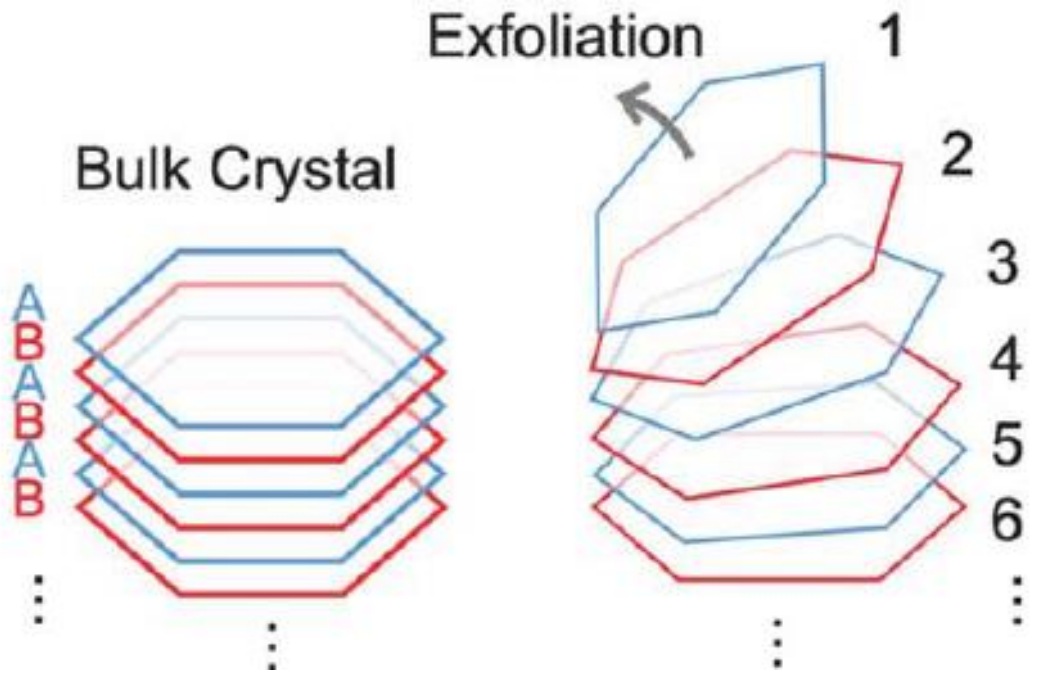
DEFINITION:

[...] layered materials with strong in-plane bonds and weak, van der Waals-like coupling between layers.

Novoselov et al. PNAS, 102, 30 (2005)



Yao, J.D. et al., Prog.Mat.Sc., 106 (2019)



F.Liu et al. Science, 367 (2020)

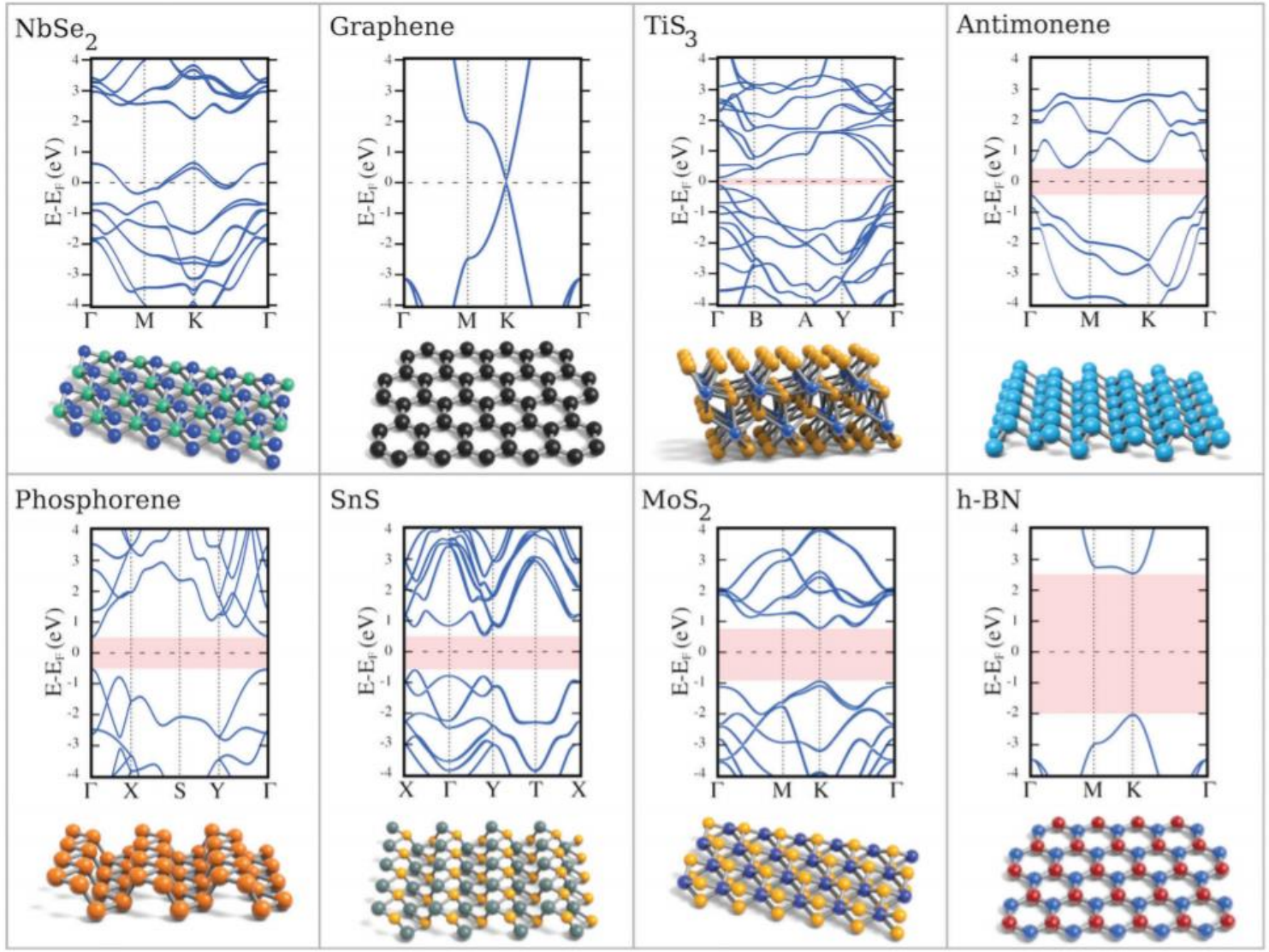
VdW Materials = 2D Crystals

DEFINITION:

Dimensionality is one of the most defining material parameters; the same chemical compound can exhibit dramatically different properties depending on whether it is arranged in a 0D, 1D, 2D, or 3D crystal structure. Although quasi-0D [e.g., cage molecules (**1**)], quasi-1D [e.g., nanotubes (**2**-**4**)], and, of course, 3D crystalline objects are well documented, dimensionality two is conspicuously absent among experimentally known crystals. On the other hand, there are many layered materials with strong in-plane bonds and weak, van der Waals-like coupling between layers. Because of this layered structure, it has long been tempting to try splitting such materials into individual atomic layers, although it remained unclear whether free-standing atomic layers could exist in principle [thin films become thermodynamically unstable (decompose or segregate) below a certain thickness, typically, of many dozens layers].

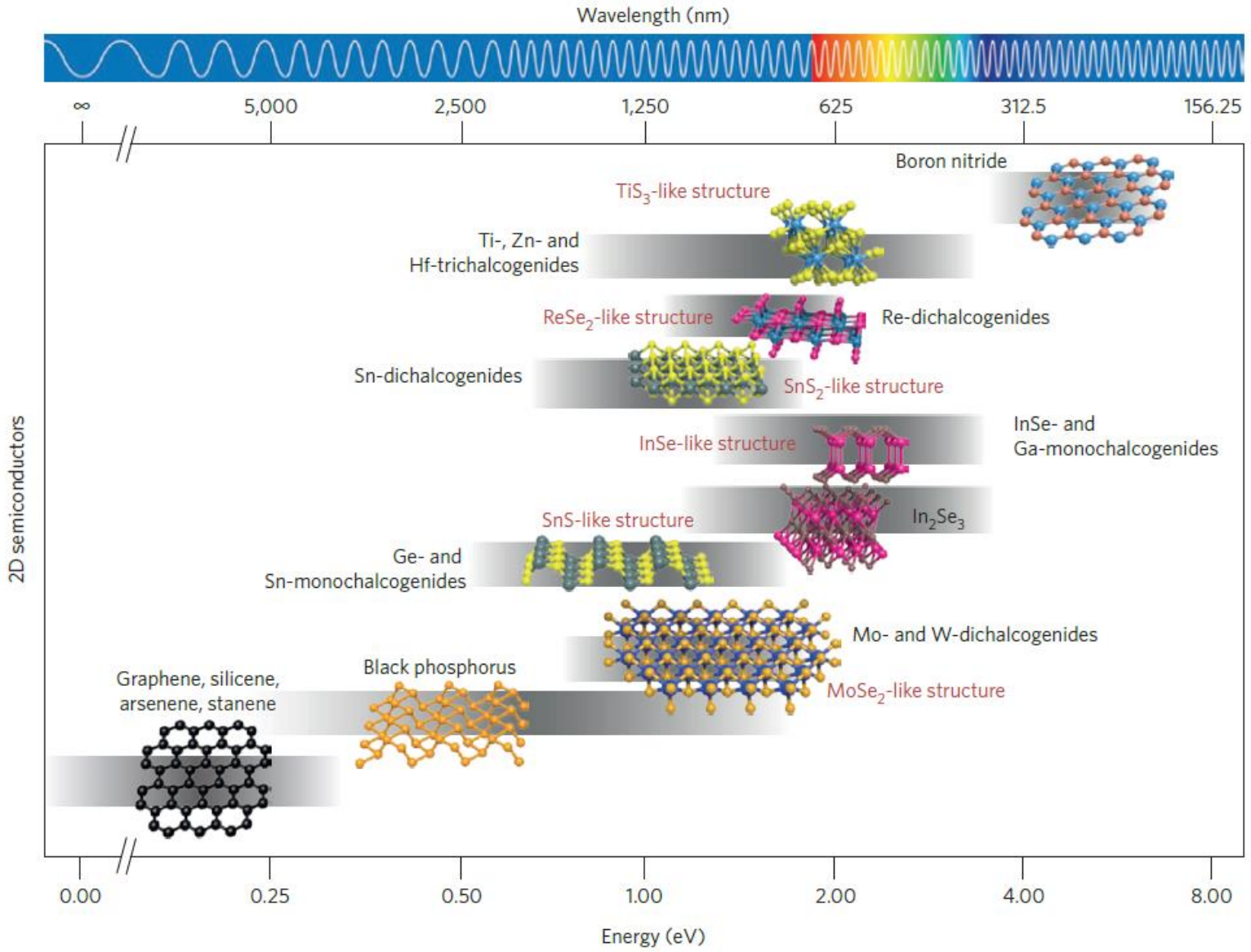
Novoselov et al. PNAS, 102, 30 (2005)

Van der Waals Compounds



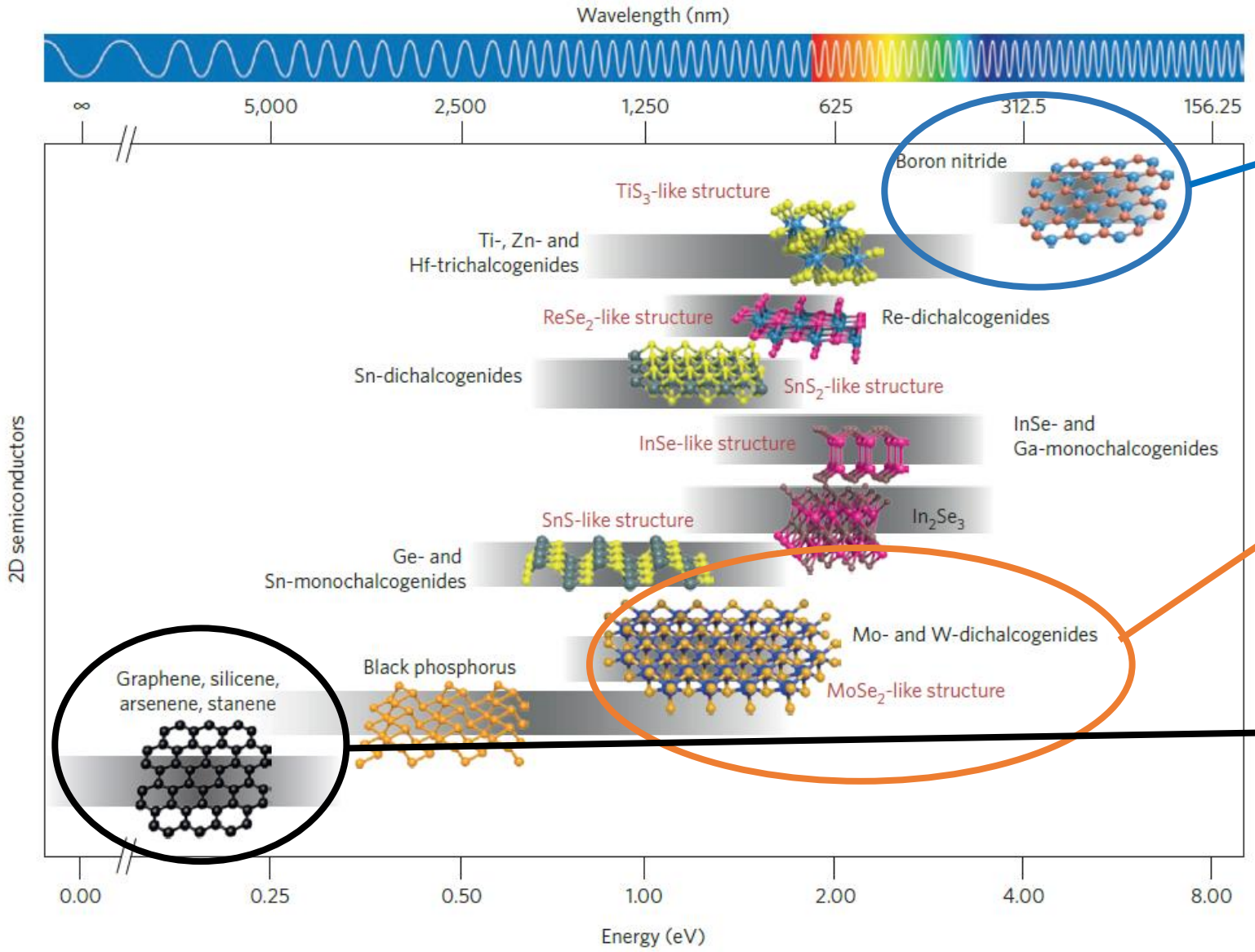
Castellanos-Gomes, Nature Photonics, 10, (2016)

Van der Waals Compounds

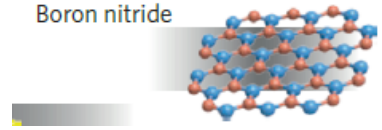


Castellanos-Gomes, Nature Photonics, 10, (2016)

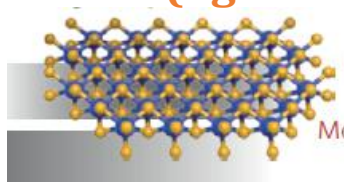
Van der Waals Compounds



Boron Nitride (BN) (Eg~ 4 eV)

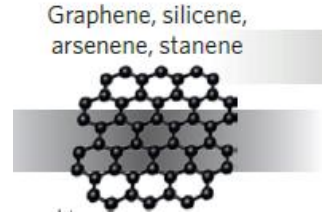


Transition Metal Dichalcogenides (Eg~ 1-2 eV)



Mo-, W-
-S, -Se

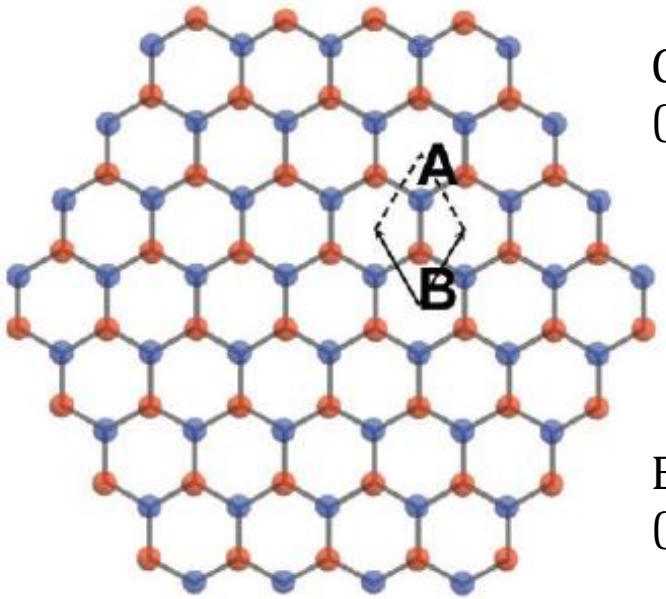
Graphene



Castellanos-Gomes, Nature Photonics, 10, (2016)

Crystal structure (1)

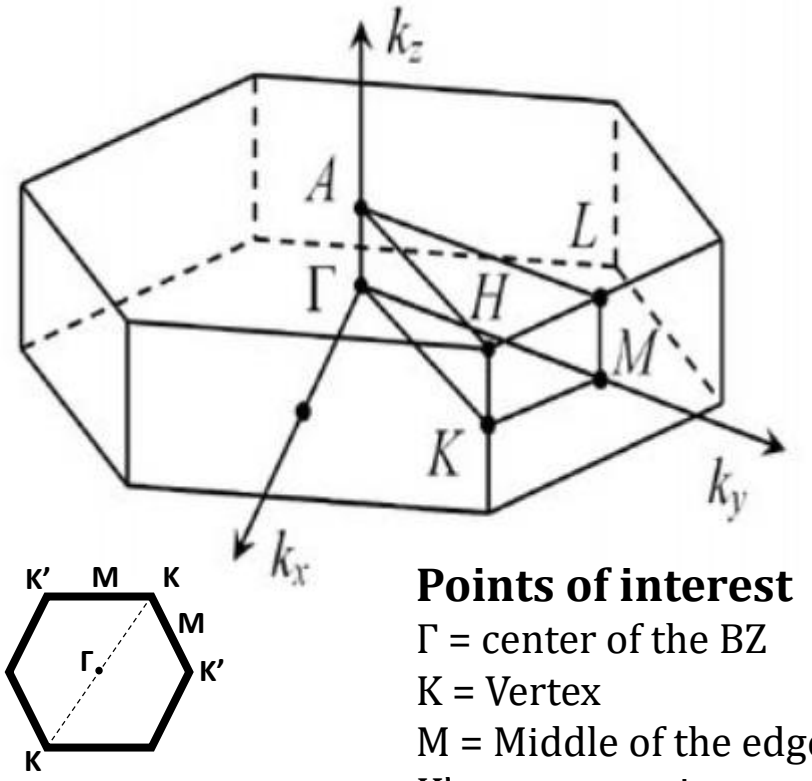
Planar atomic layer = sp^2 hybridization = **<u>hexagonal lattice</u>**



Graphene
(atomic compound)

BN*
(bi-atomic compound)

<u>Brillouin Zone</u>



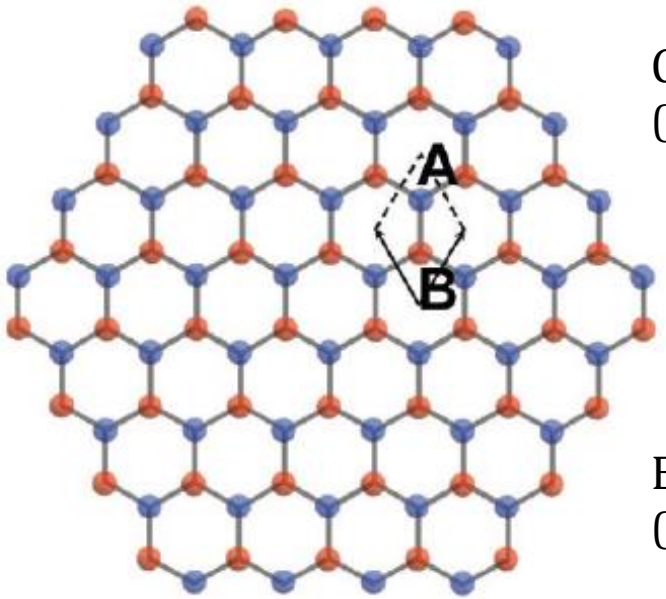
Points of interest
Γ = center of the BZ
K = Vertex
M = Middle of the edge
K' = asymmetric vertex

<u>*Avouris, NanoLetter, 10, (2010)*</u>

* Additional 3D phases exist, such as cubic BN (sp^3 hybridization). To differentiate the phases, the 2D crystal is often named «h-BN»

Crystal structure (1)

Planar atomic layer = sp^2 hybridization = **<u>hexagonal lattice</u>**



Graphene
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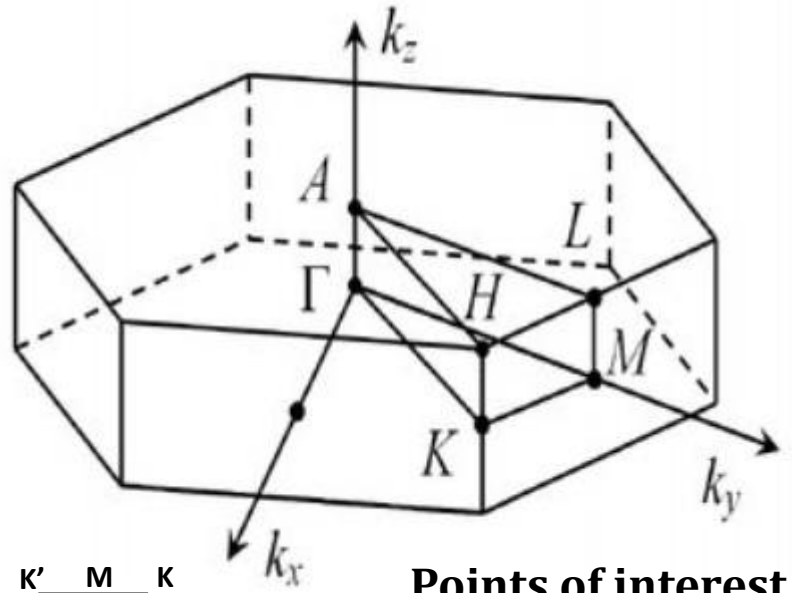
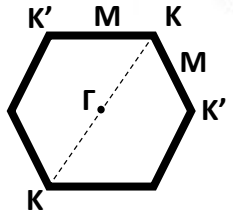
<u>Brillouin Zone</u>





Points of interest
Γ = center of the BZ
K = Vertex
M = Middle of the edge
K' = asymmetric vertex

Which of these compounds present a K' point in its BZ?

* Additional 3D phases exist, such as cubic BN (sp^3 hybridization). To differentiate the phases, the 2D crystal is often named «h-BN»

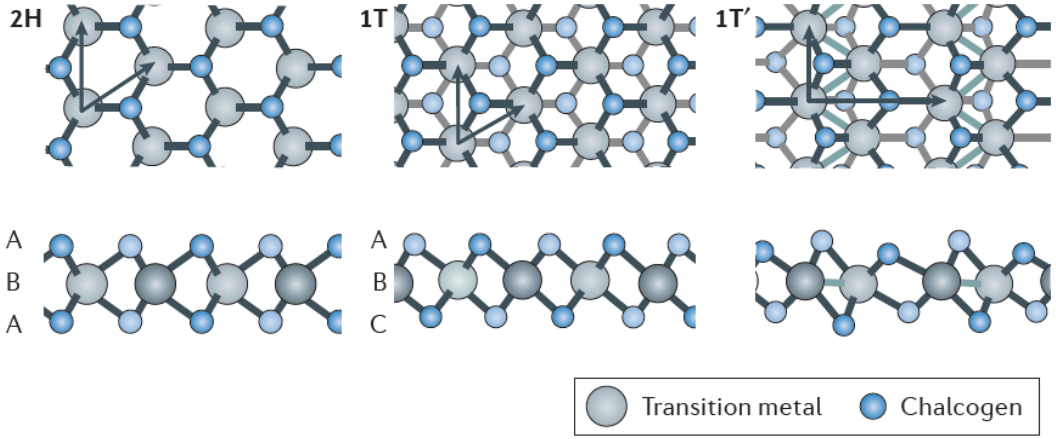
<u>Avouris, NanoLetter, 10, (2010)</u>

Crystal structure (2)

Transition Metal Dichalcogenides (TMDs) Formula: MX_2

M = Metal (W, Mo, Nb, Ti...)
X = Chalcogen (S, Se or Te)

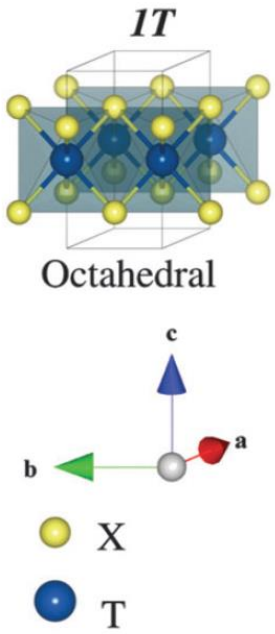
Lattice depends on the coordination of the metal atom.

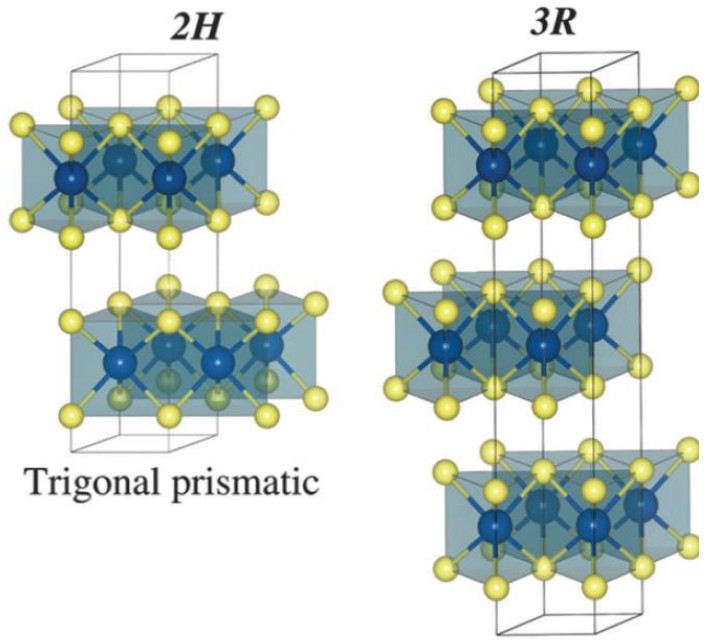


Trigonal prismatic *Octahedral* *Dimerized*

1T, 2H, 3R
Number of layers in the unit
+
Letter denotes the symmetry

(Hexagonal Lattice)





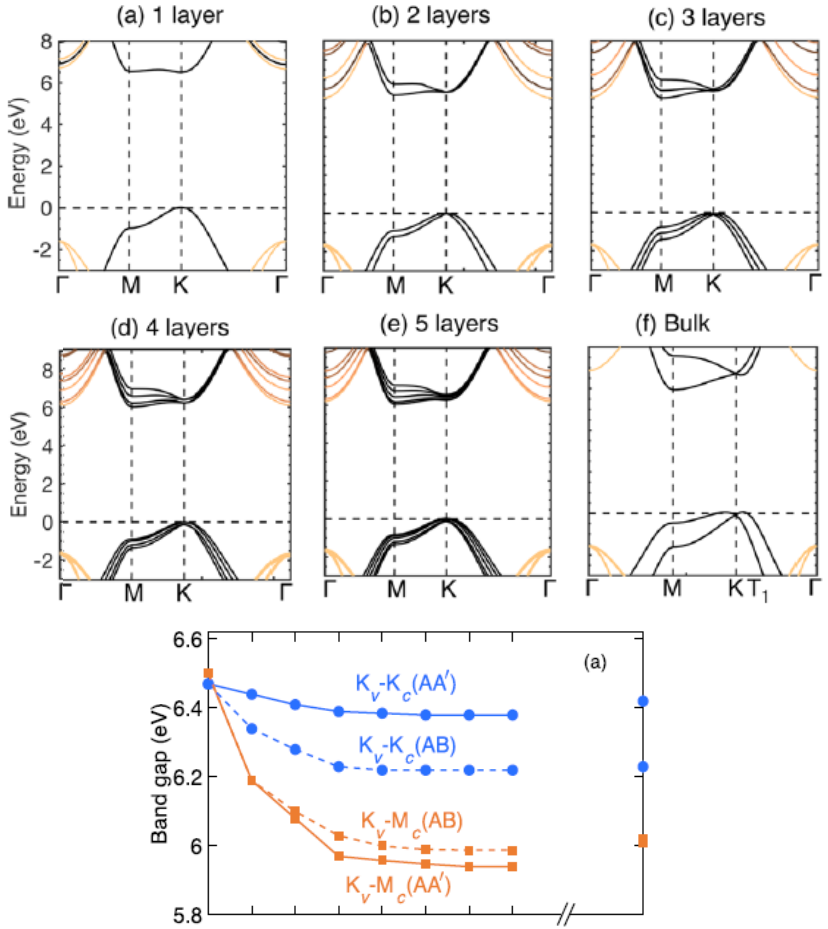
Thermodynamically Stable Phases for: MoS_2 WS_2 $MoSe_2$ WSe_2

Manzeli et al., Nature Reviews, 2, (2017)

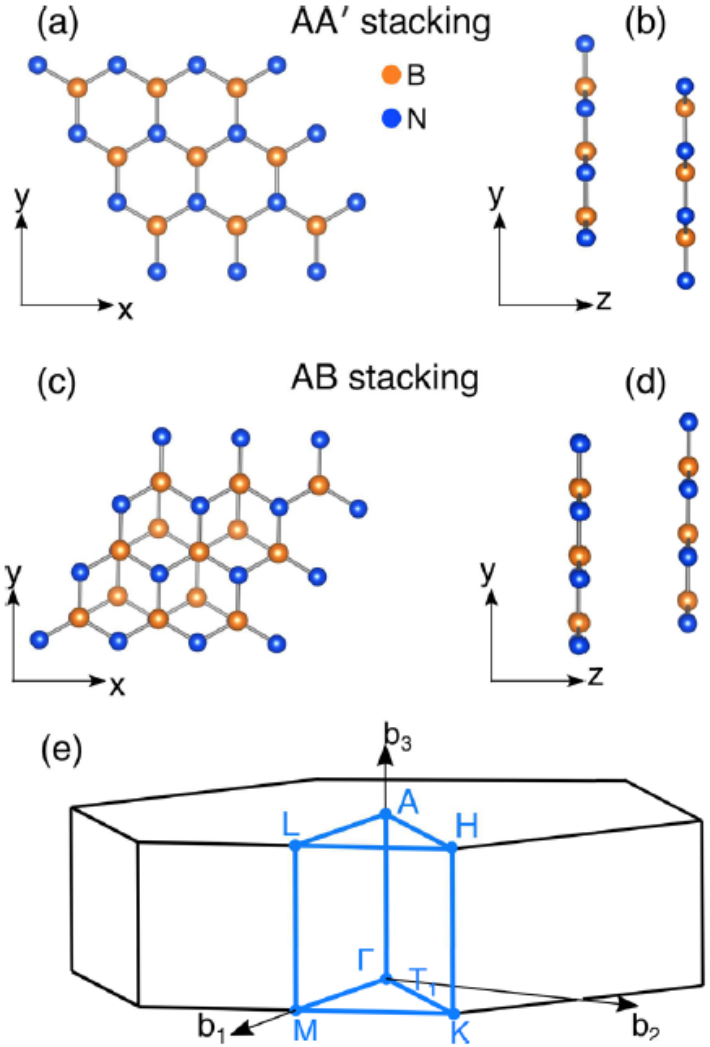
Kuc et al., Chem. Soc. Rev., 44 (2015)

Unique Features

Layer-dependance



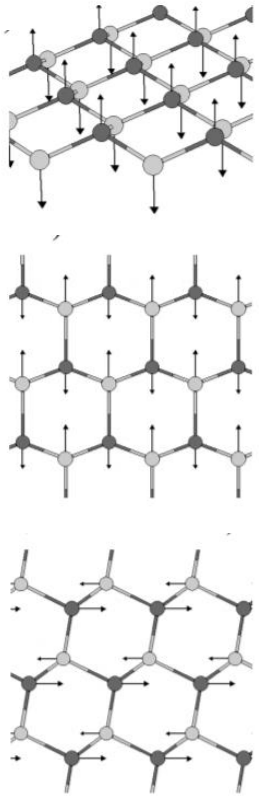
Sequencing



Wickramaratne et al. J. Phys. Chem. C, 122, (2018)

Bulk to monolayer: lattice vibration

Example of vibrational modes (h-BN)

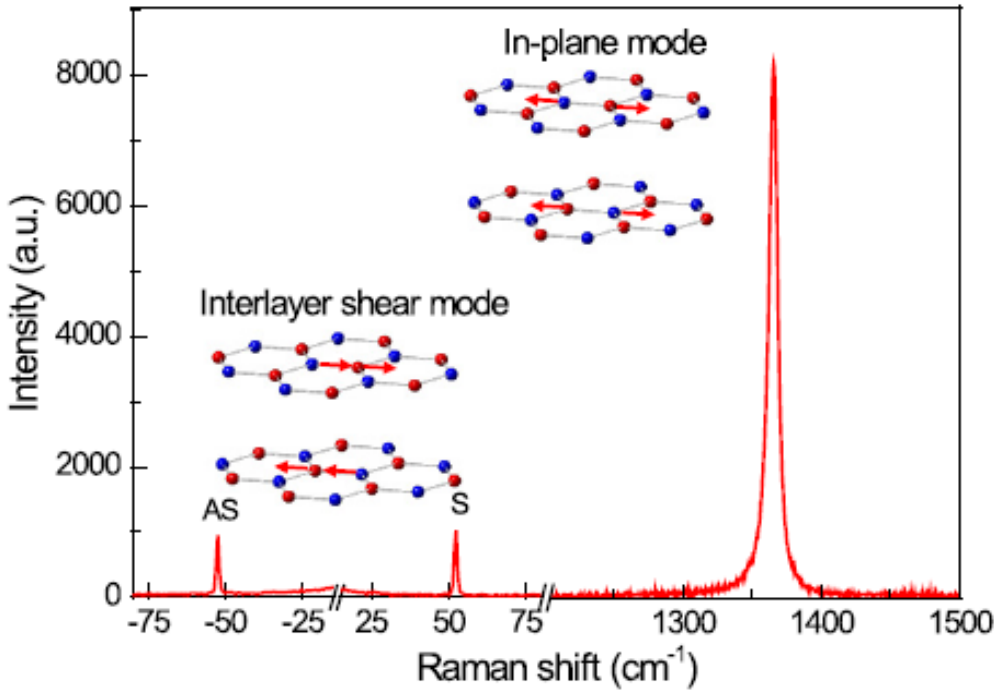


Out-of-plane

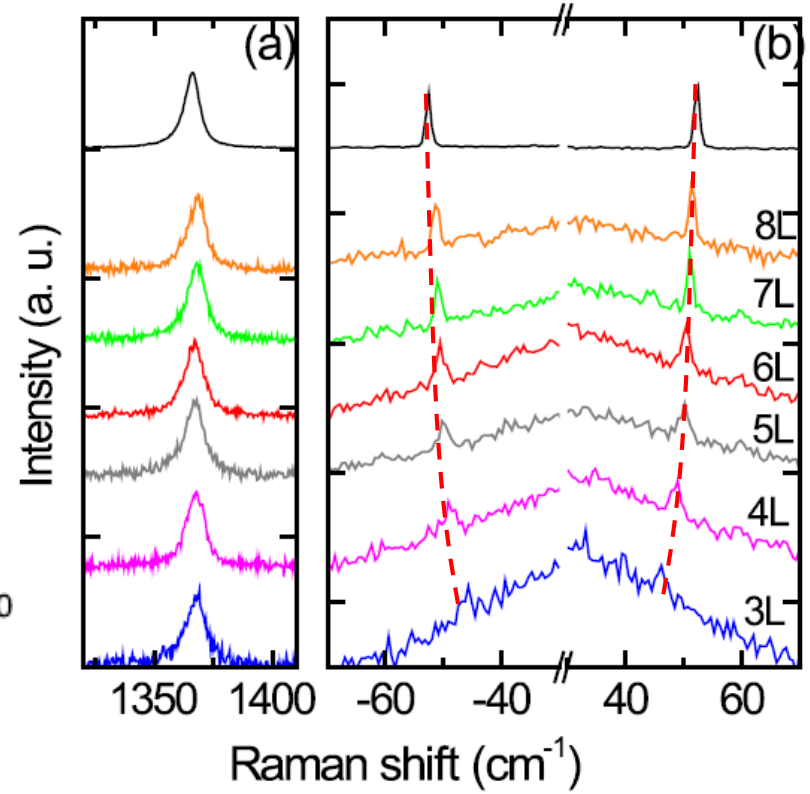
In-plane (Transverse)

In-plane (Longitudinal)

Bulk h-BN



Decreasing number of layers (L)



No significant variation on in-plane mode Raman peak at ~1350 cm^{-1}

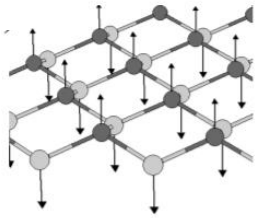
Significant shift of the shear mode Raman peak at ~ 50 cm^{-1}

Wirtz et al., PRB, 68, (2003)

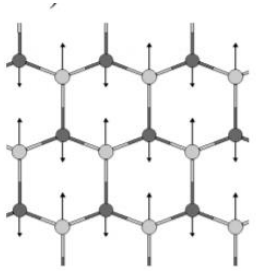
Stenger et al., 2D Mater., 4, (2017)

Bulk to monolayer: lattice vibration

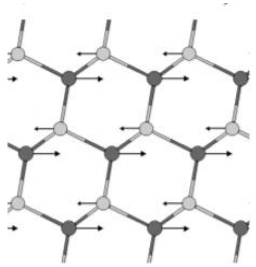
Example of vibrational modes (h-BN)



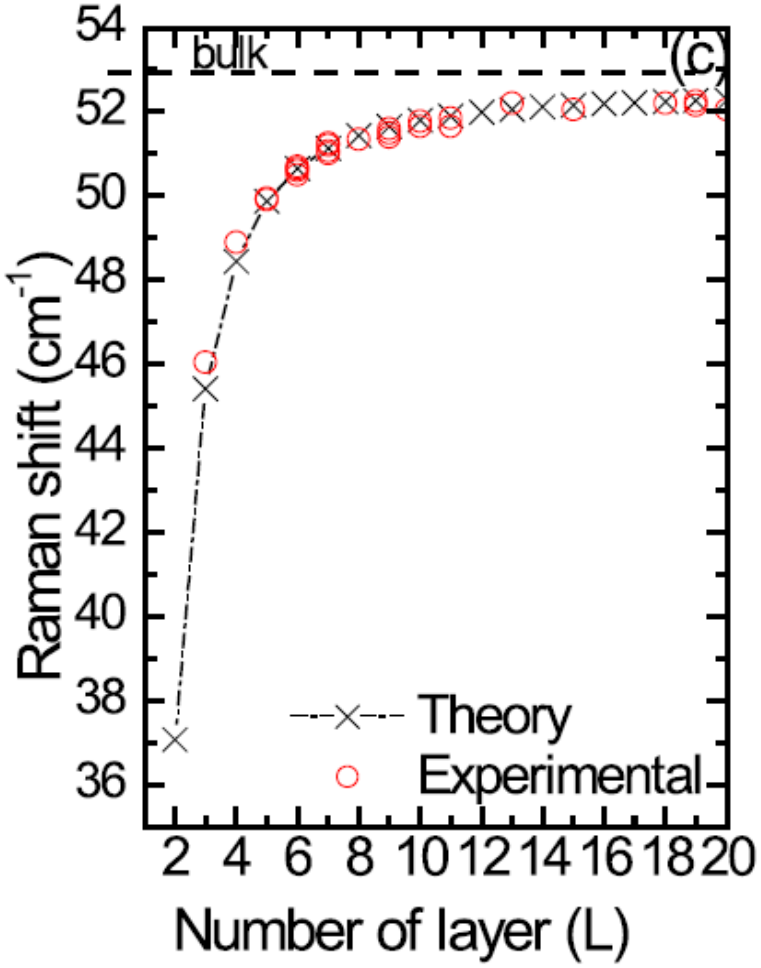
Out-of-plane



In-plane (Transverse)



In-plane (Longitudinal)



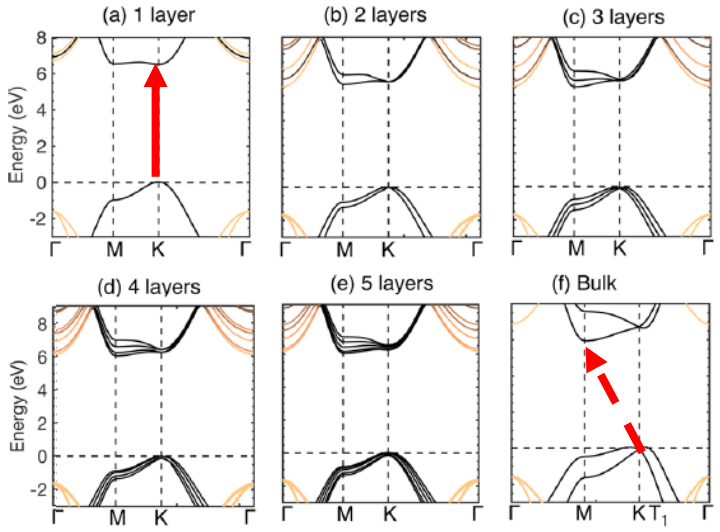
Theoretical estimation is done through a linear chain model (each layer interacts only with the adjacent ones)

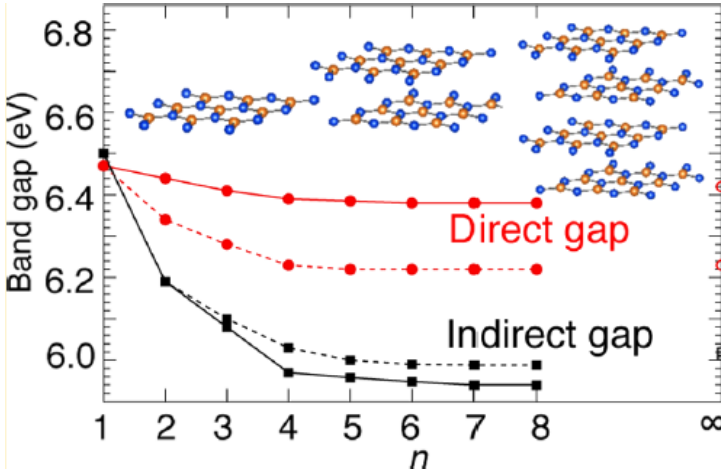
Wirtz et al., PRB, 68, (2003)

Stenger et al ., 2D Mater., 4, (2017)

Bulk to monolayer: band structure (1)

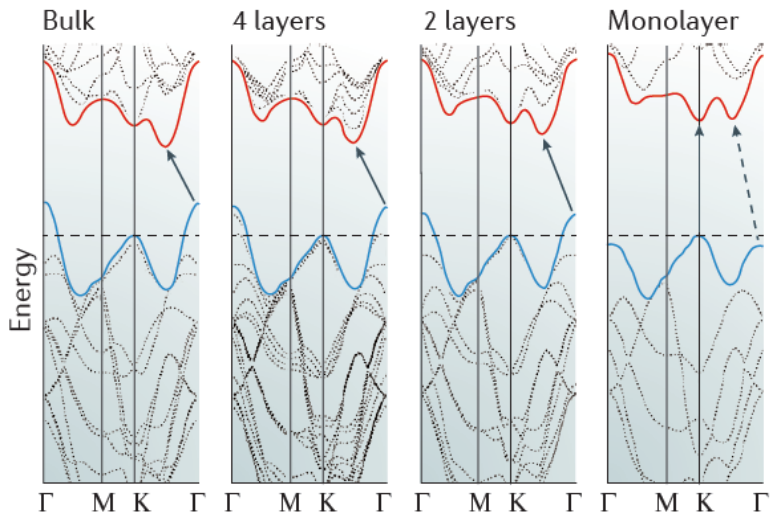
h-BN

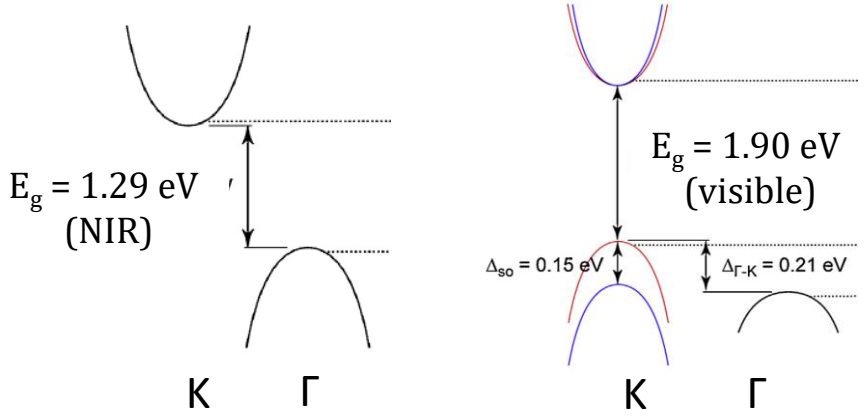




Wickramaratne et al. J. Phys. Chem. C, 122, (2018)

MoS_2



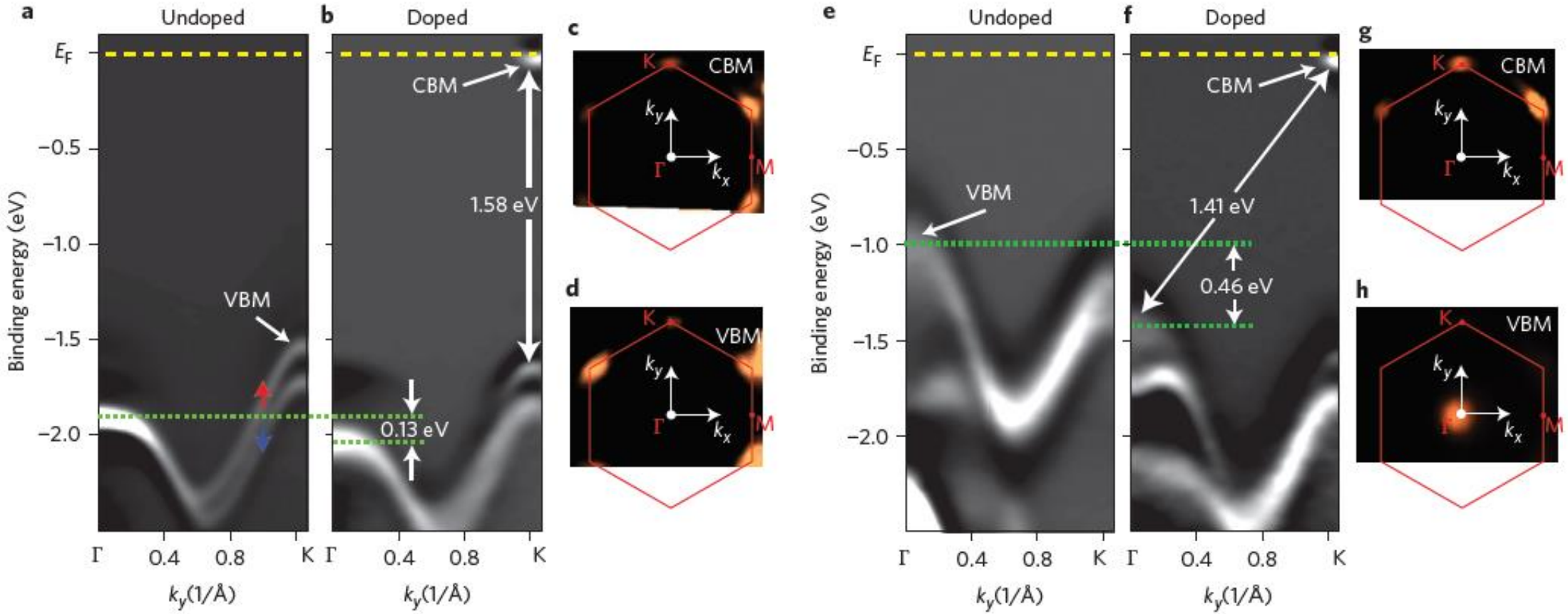


Manzeli et al., Nature Reviews, 2, (2017)

Yazyev, A. Kis, Mater. Today, 18, (2014)

Bulk to monolayer: band structure (2)

Angle Resolved PhotoEmission Spectroscopy (ARPES)



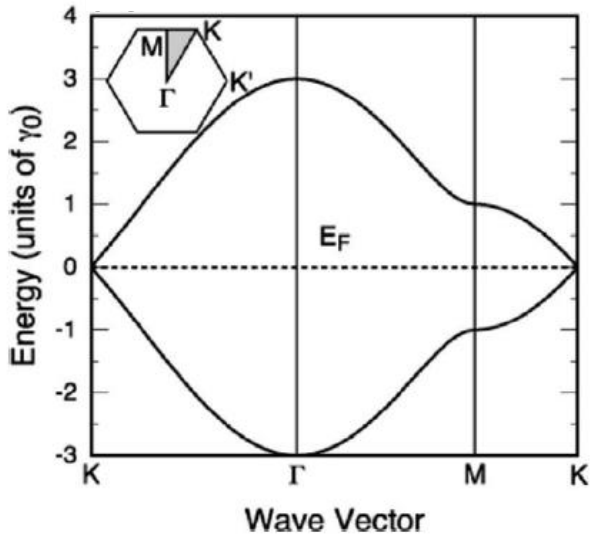
1 ML - $MoSe_2$

8 ML - $MoSe_2$

Zhang et al., Nature Nanotech, 9, (2014)

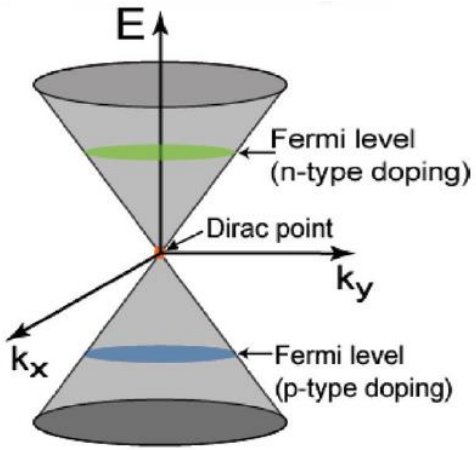
Bulk to monolayer: band structure (3)

Graphene

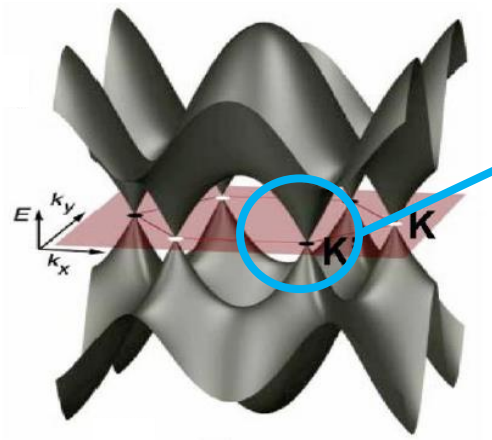


E_g = 0 eV at K points (high symmetry)

Metal behaviour

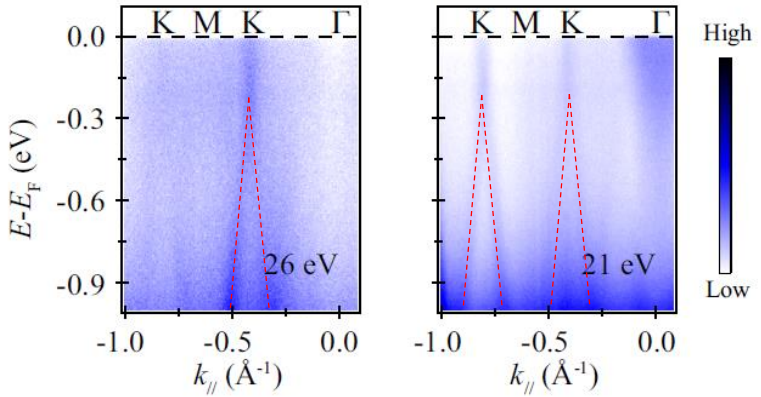


DIRAC CONE:
Linear energy – momentum relationship (E-k)



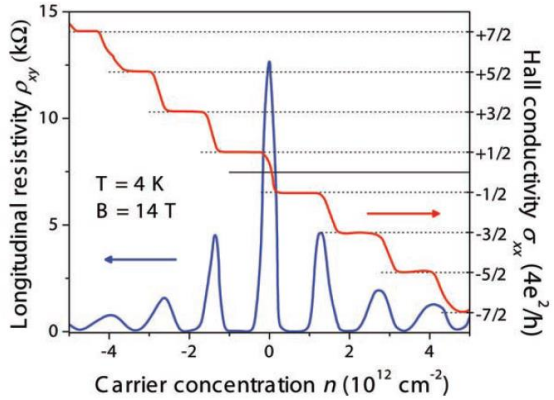
Avouris, NanoLetter, 10, (2010)

ARPES measurements



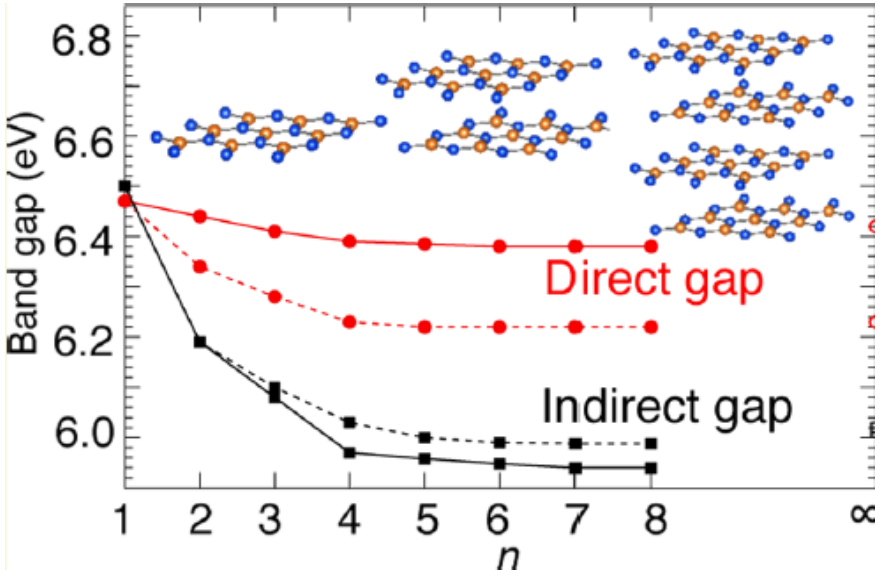
Yue, PRB, 108, (2020)

QHE in Dirac Cones



Weiss, Adv. Mater., 24, (2012)

Exercise (10 minutes)



Why in 2D crystals the band gap is decreasing with increasing number of layers?

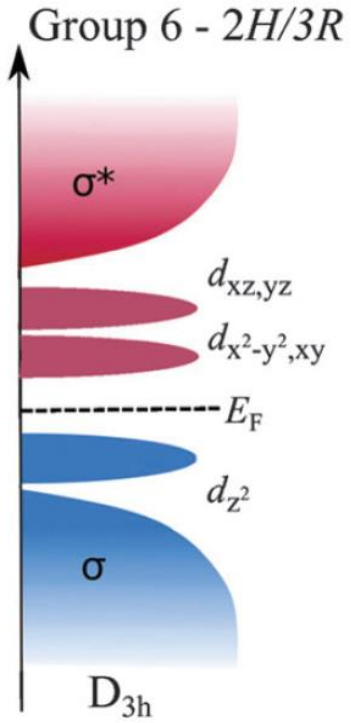
Why are there 4 curves to indicate direct and indirect band gaps of h-BN?

Exercise (5 minutes)

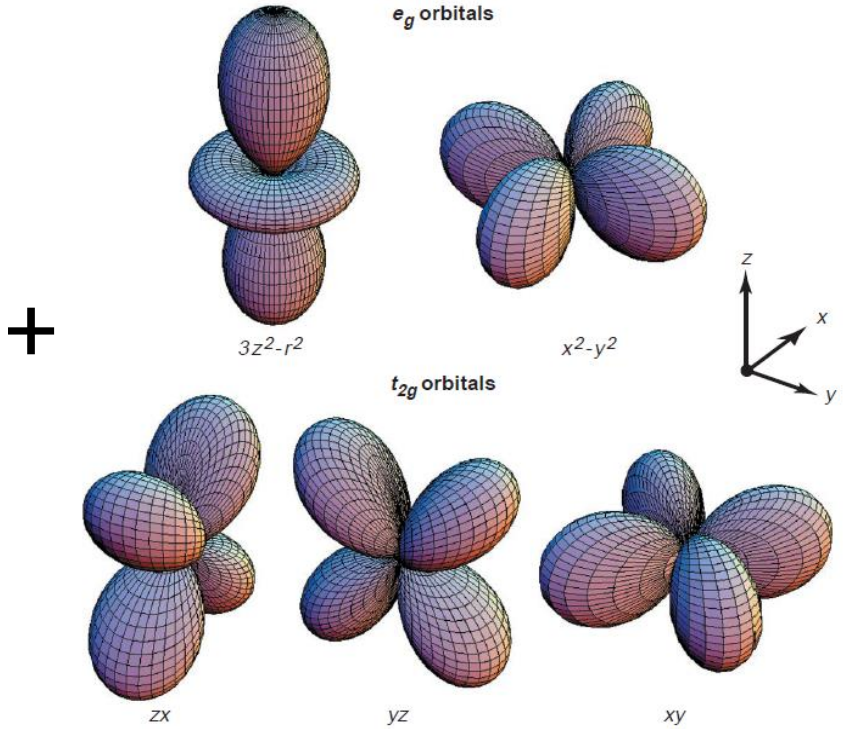
To be solved in Class

Effect of spin-orbit interaction on energy bands

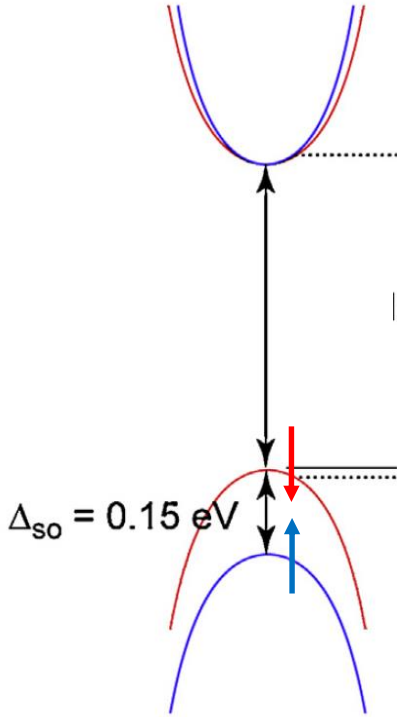
Conduction and Valence band lower levels consists of d-orbitals



D-orbitals have a high angular momentum



Valence band split off



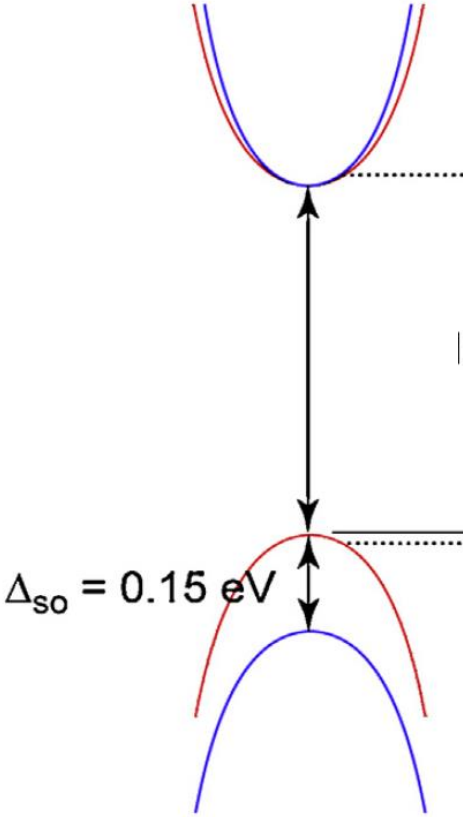
The split off is due to the spin-orbit of the electrons in the VB

Kuc et al., Chem. Soc. Rev., 44 (2015)

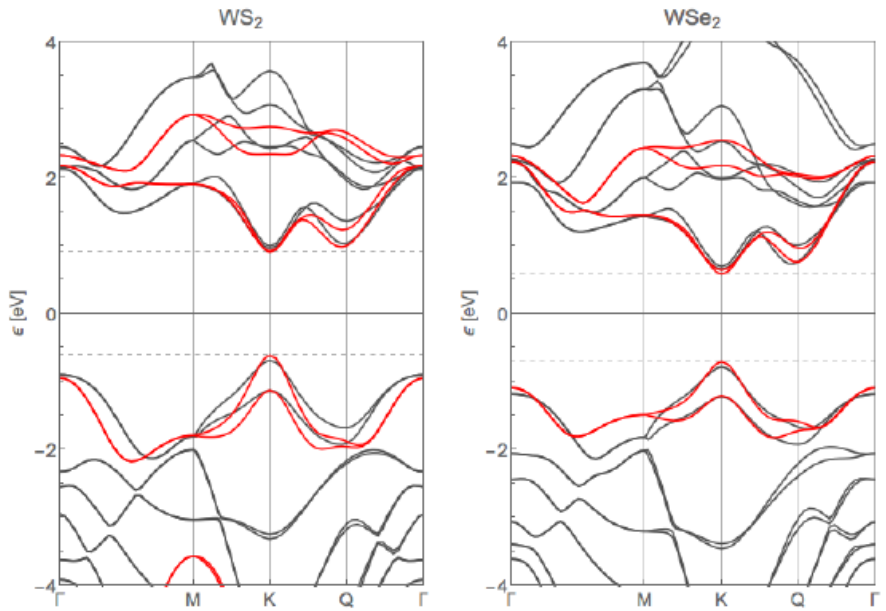
Tokura et al., Science., 288 (2000)

Yazyev, A. Kis, Mater. Today, 18, (2014)

From spin-orbit interaction to spintronic



WS_2 and WSe_2



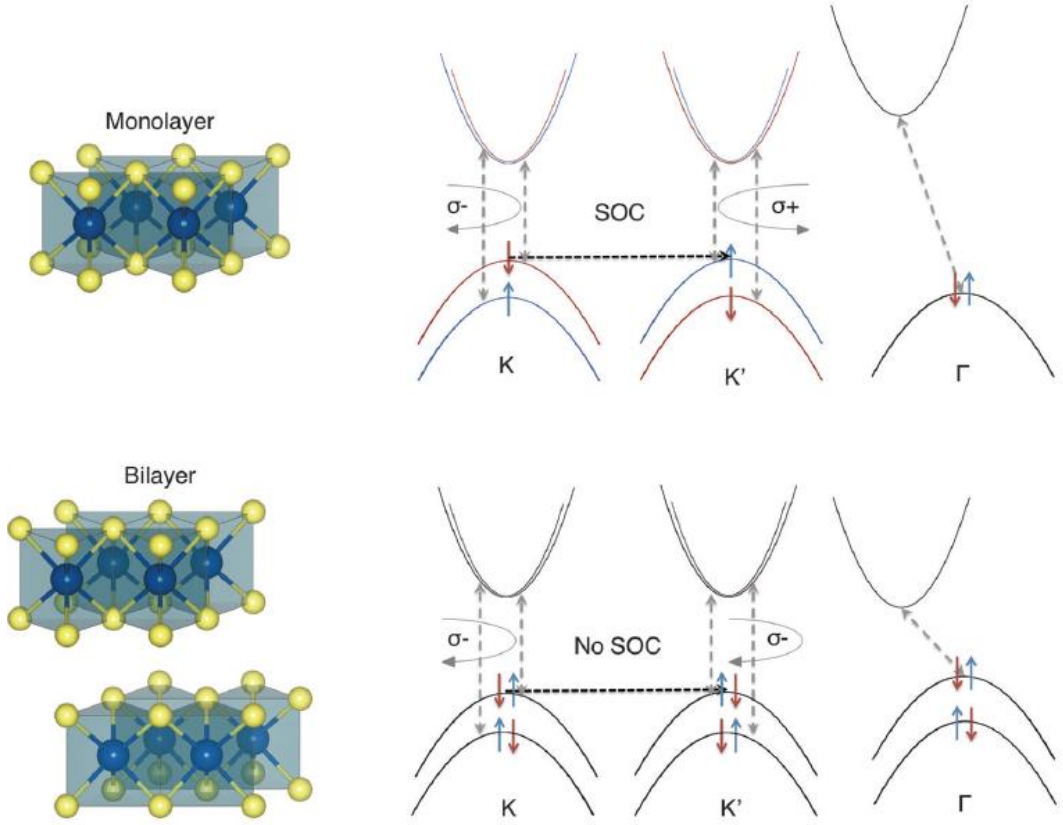
Spintronic: engineering spin split-off by applying external electric and magnetic fields.

Requirement: Materials with high spin-orbit interaction, i.e. materials exhibiting valence split off due to the coupling/decoupling between spin and orbitals

Kuc et al., Chem. Soc. Rev., 44 (2015)
Silva-Guillén et al., Appl. Sci. 6,284, (2016)

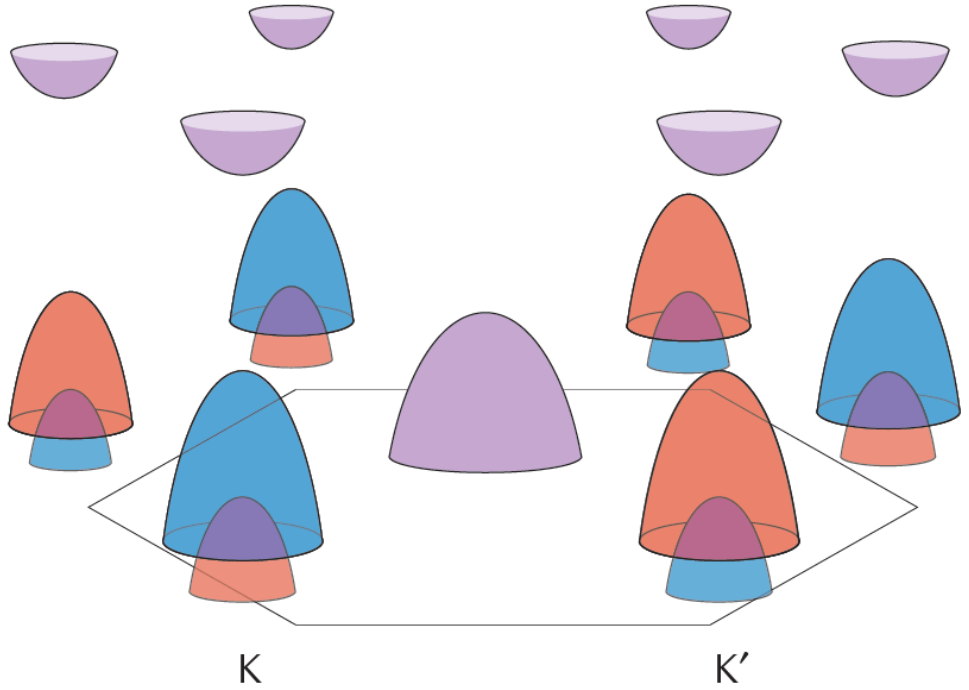
From spintronic to valleytronic

Effect of inversion symmetry on the spin-orbit coupling.



Polarization dependent selection rule for light absorption

Spin-Valley Locking



Valleytronic: engineering functional properties on the base of valley-related spin-orbit coupling.

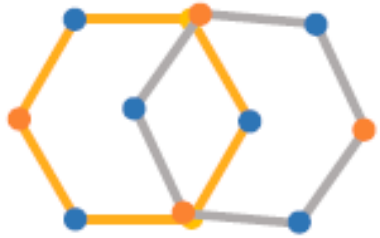
Kuc et al., Chem. Soc. Rev., 44 (2015)

Manzeli et al., Nature Reviews, 2, (2017)

Layer sequencing: 2D stackings

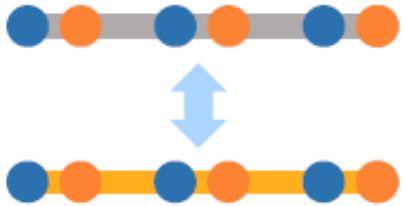
Multi-layer configurations

AA ($\theta = 0°$)



Twsit ($\theta = 5°$)

AB ($\theta = 60°$)



Parallel Stacking
AA Configuration

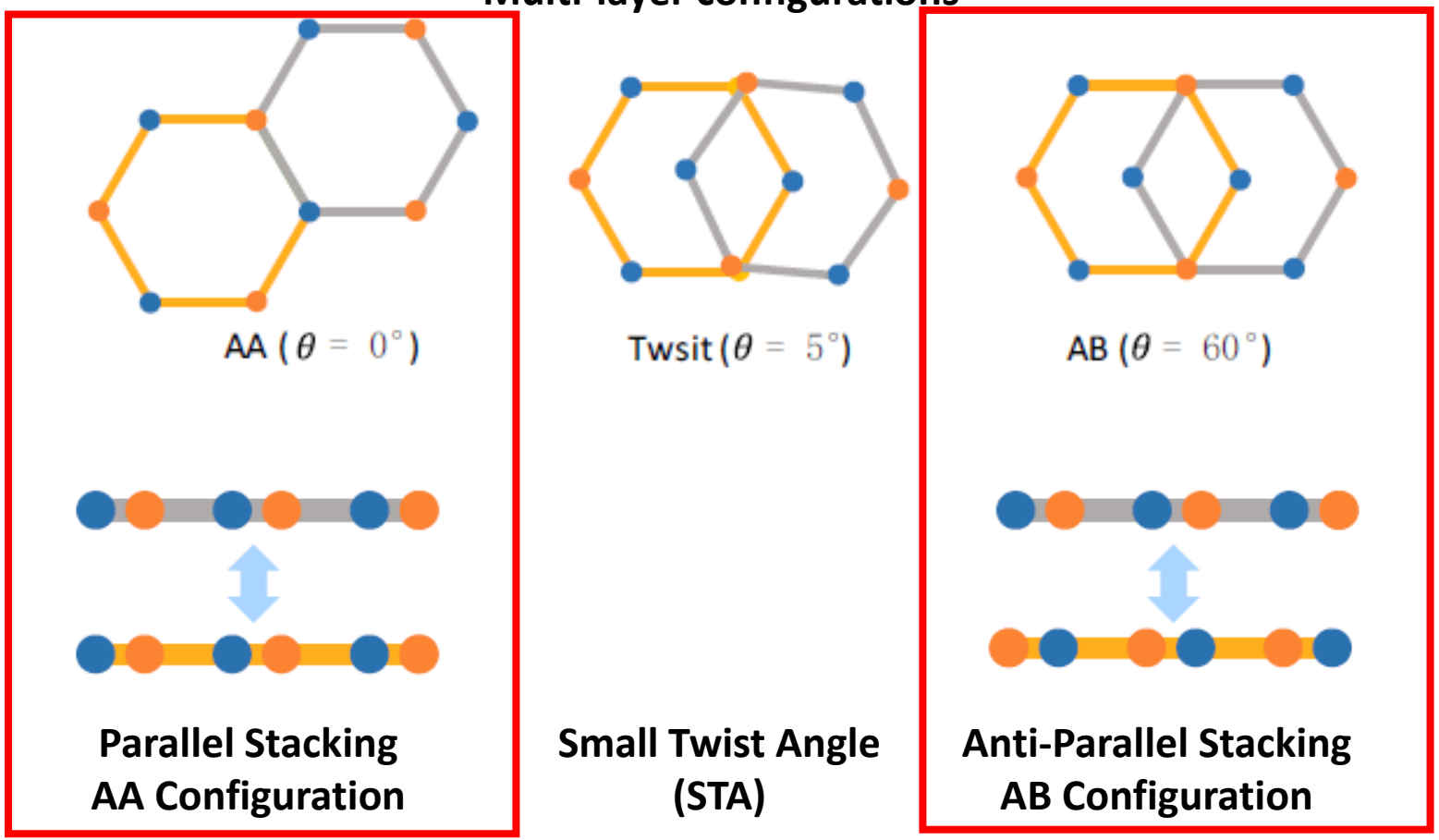
Small Twist Angle
(STA)

Anti-Parallel Stacking
AB Configuration

Cheng et al., Chin. Phys. B, 28, (2019)

Layer sequencing: 2D stackings

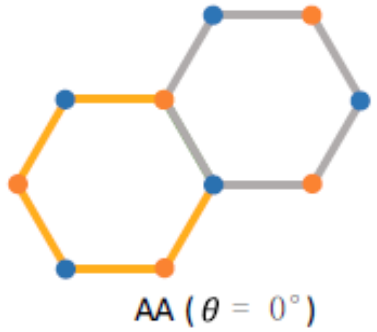
Multi-layer configurations



Cheng et al., Chin. Phys. B, 28, (2019)

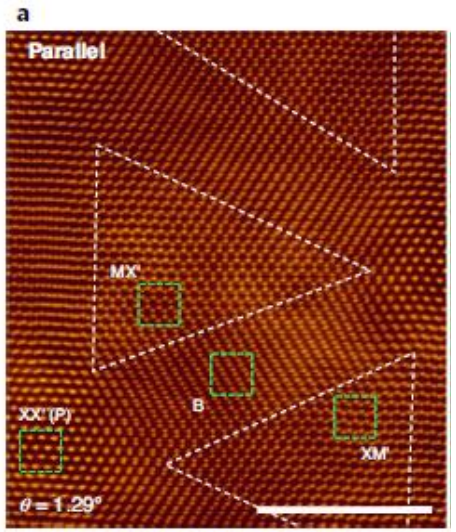
Layer sequencing: Parallel Stacking

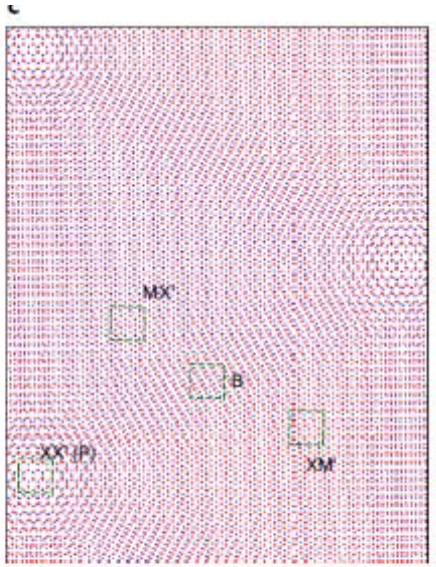
Parallel configuration (AA)

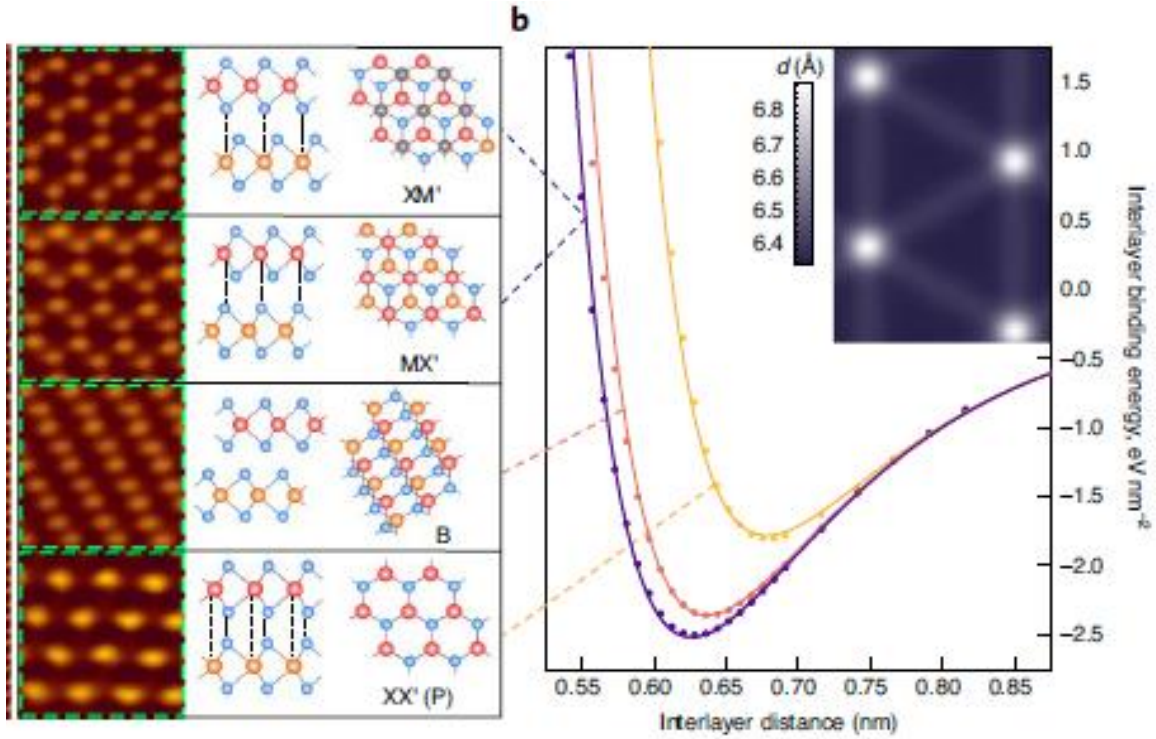


WS_2 Parallel Bilayer (θ = 0°)

Calc.







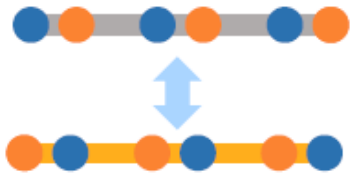
Cheng et al., Chin. Phys. B, 28, (2019)

Weston et al., Nature Nanotechn., 15, (2020)

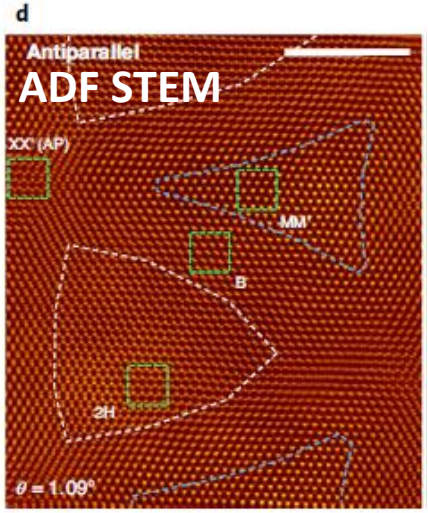
Layer sequencing: Anti-Parallel Stacking

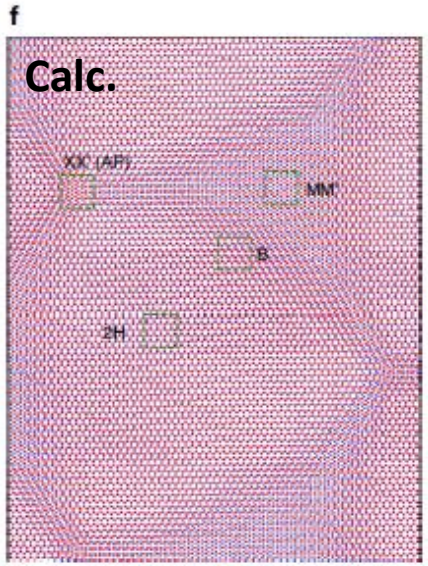
Anti- parallel configurations (AB)

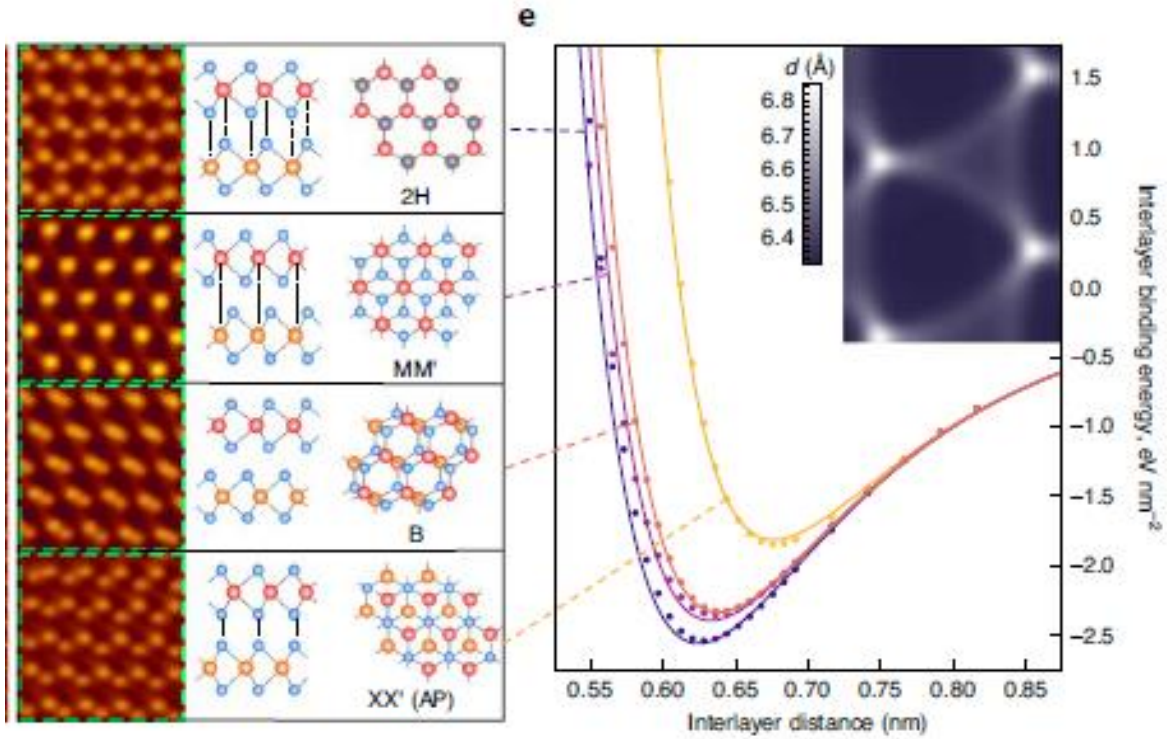
AB (θ = 60°)



WS_2 Anti-Parallel Bilayer (θ = 60°)





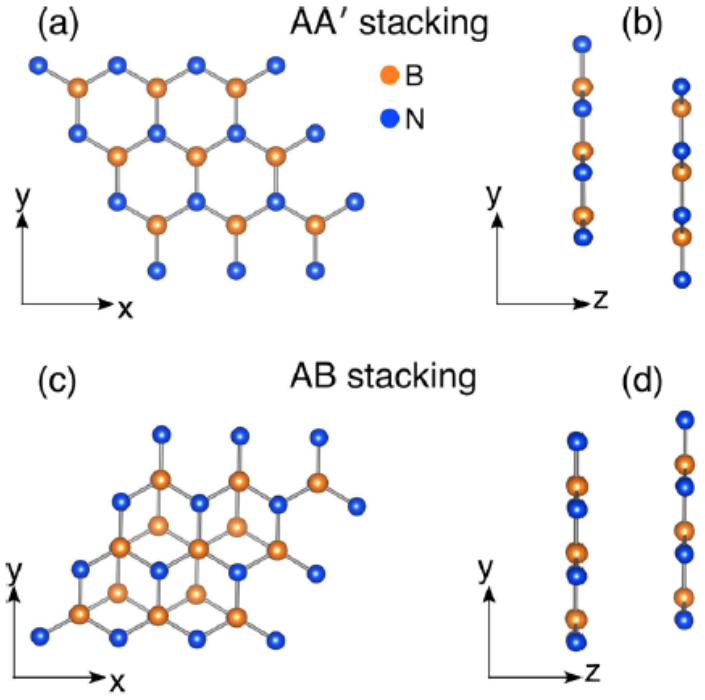


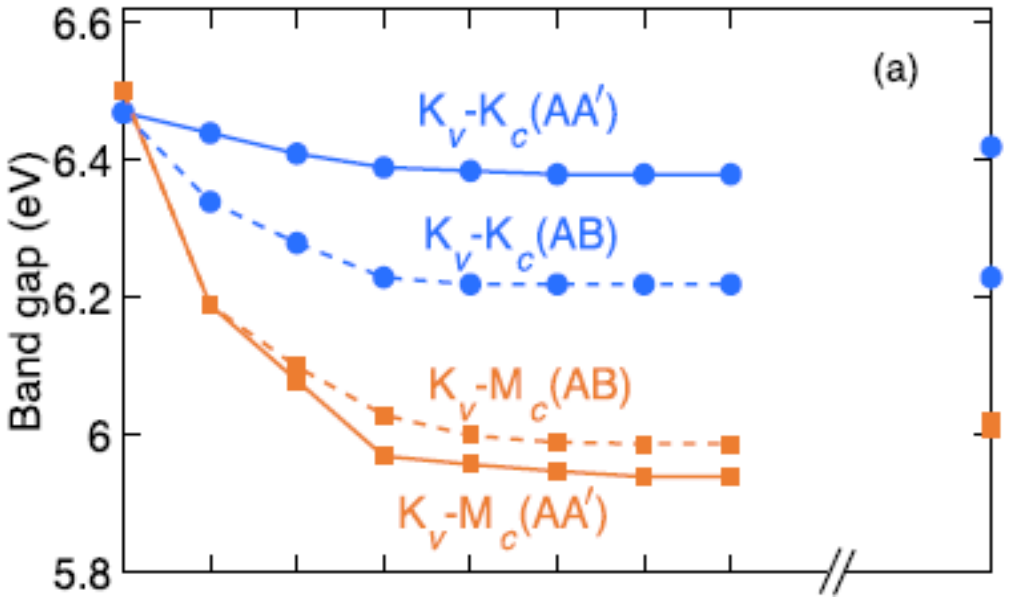
Cheng et al., Chin. Phys. B, 28, (2019)

Weston et al., Nature Nanotechn., 15, (2020)

Effect of parallel/anti-parallel stacking (1)

h-BN (previous example)



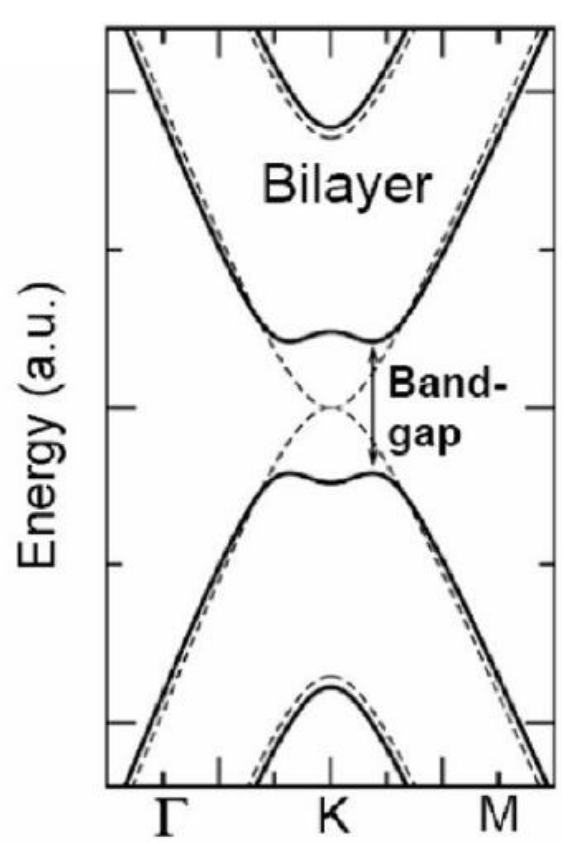


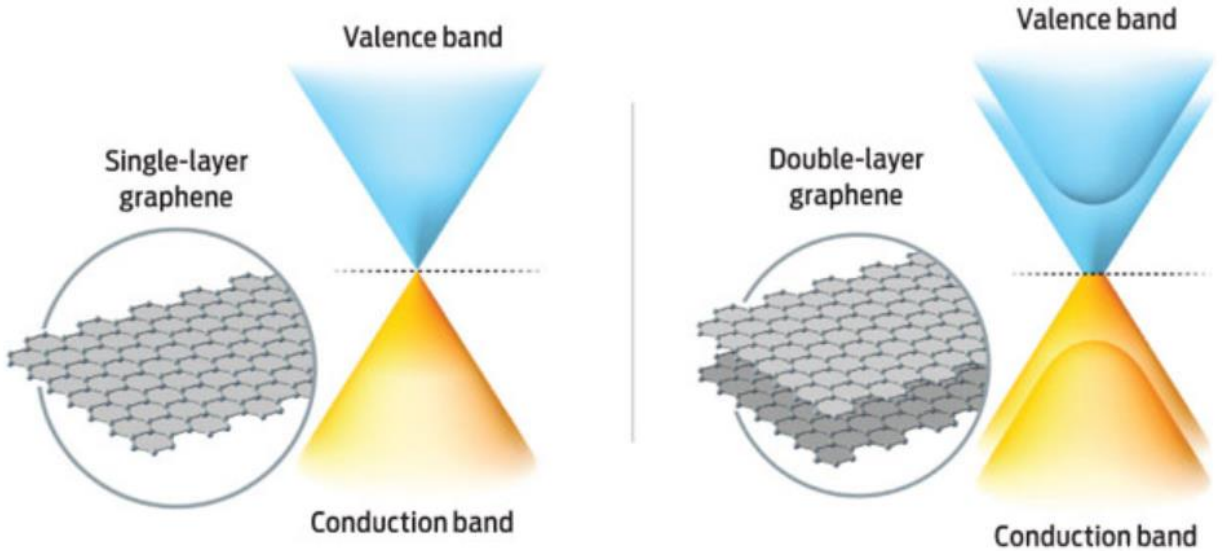
Since the interlayer distance varies with the stacking sequence, different bandgap are expected for AA' and AB configurations.

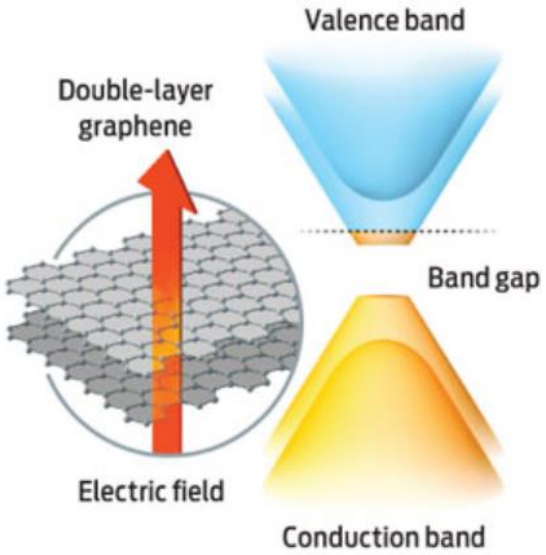
Wickramaratne et al. J. Phys. Chem. C, 122, (2018)

Effect of parallel/anti-parallel stacking (2)

Graphene







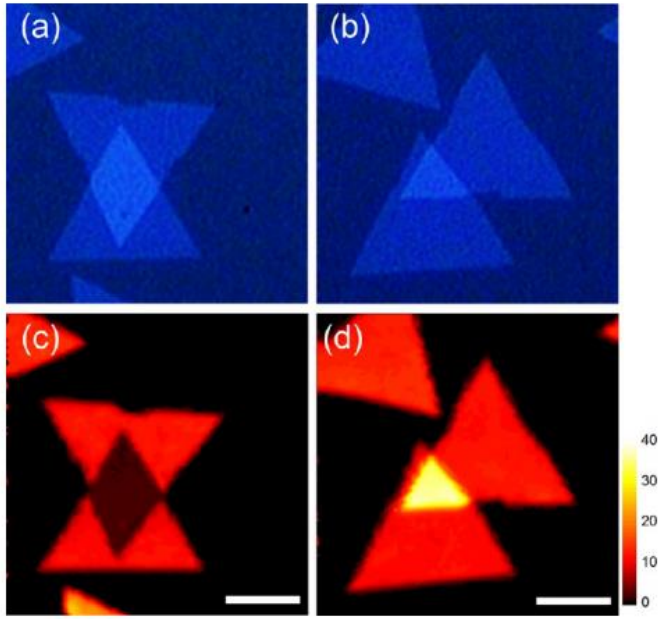
It is possible to open a band-gap in AB bilayer graphene by applying an electric field perpendicular to the layers.

McCann, Phys. Rev. B, 74 (2006)

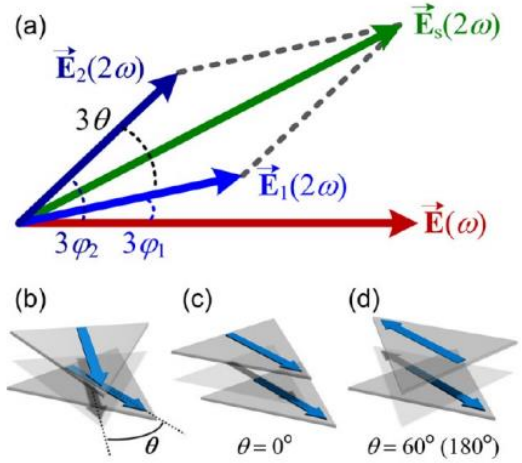
Effect of parallel/anti-parallel stacking (3)

Second Harmonic Generation

Optical microscopy image of MoS_2 flakes



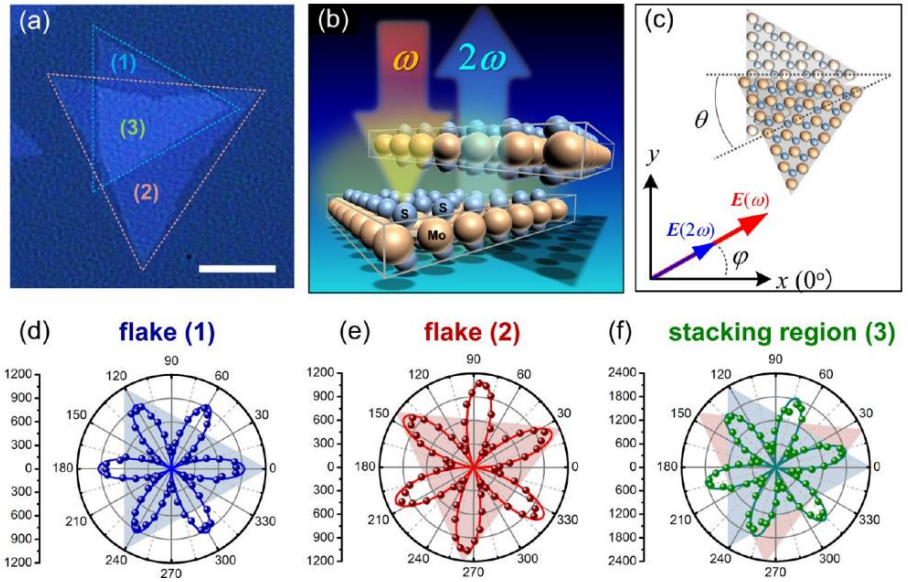
SHG map



<u>Anti-parallel</u>: Destructive interference

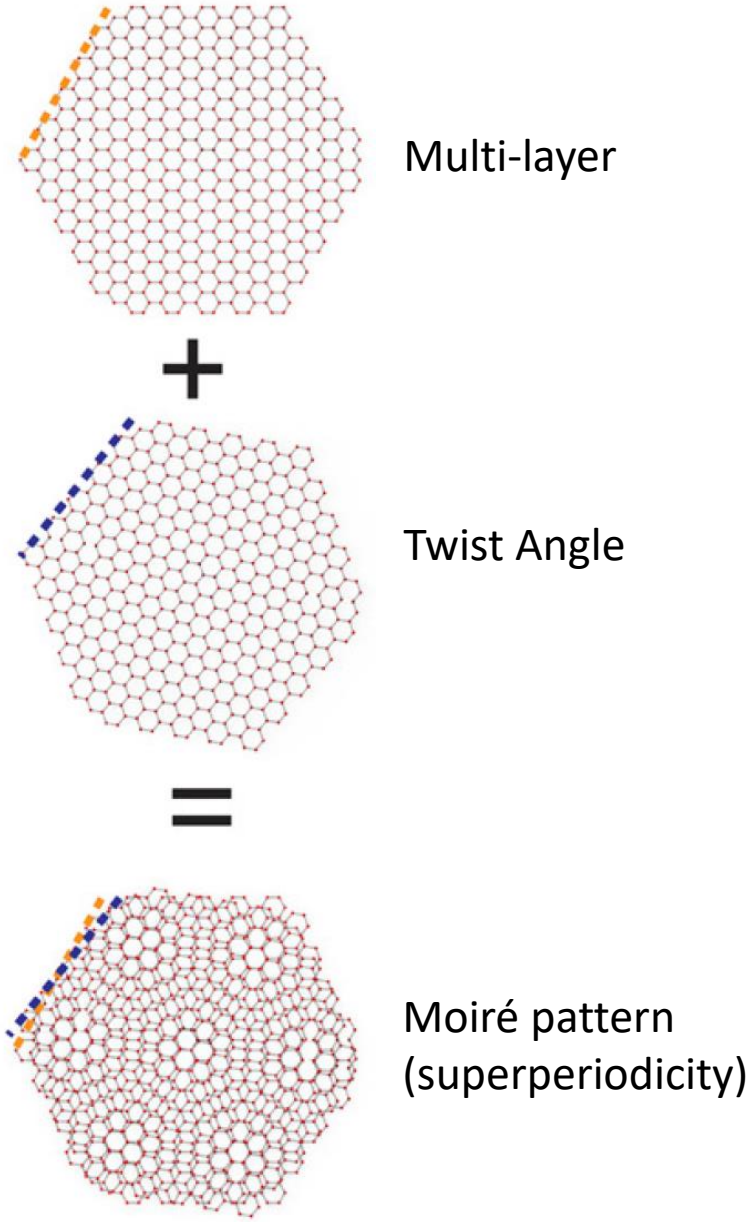
<u>Parallel</u>: Constructive interference

Polarization of SH from bilayers (Polar plot)



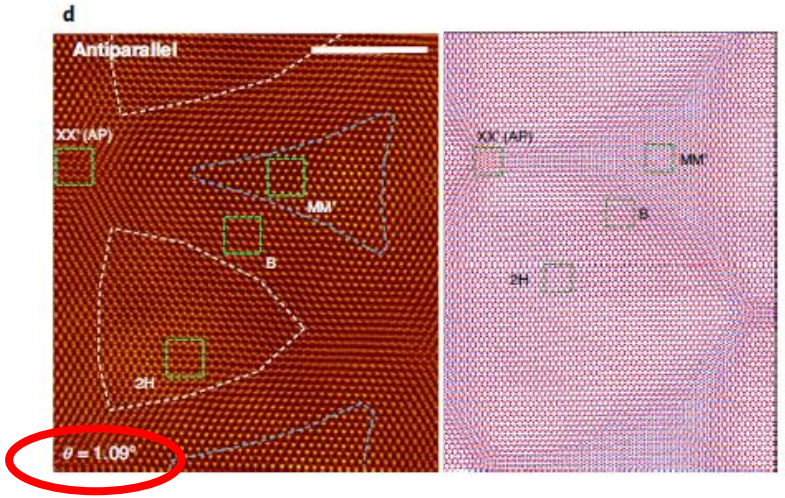
The polarization of the SH emission from a bilayer is a combination of the monolayer emission and the twisting angle

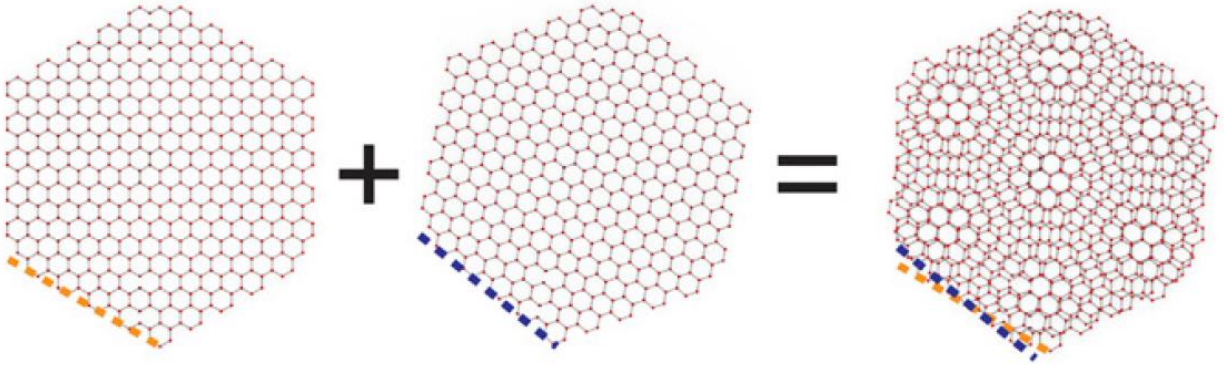
<u>Hsu et al., ACS Nano, 8 (3), (2014)</u>



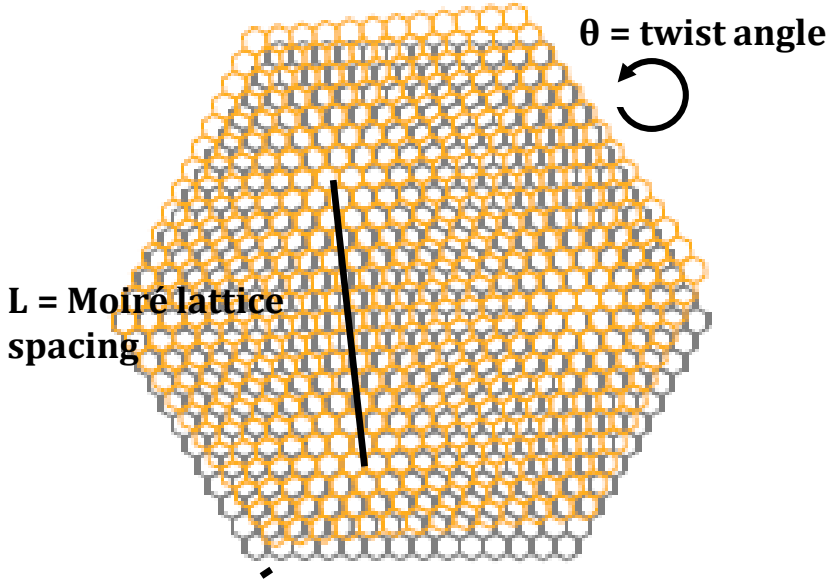
Credit to Prof. Bosco Yu, University of Victoria

Small Twisted Angle: Moiré Patterns





Moiré patterns or Moiré superlattice:
long-range ordered sequence of crystal lattices



For θ<3° (small twist angle):

$$L = \frac{a}{2\sin\left(\frac{\theta}{2}\right)}$$

Superperiodicity constant

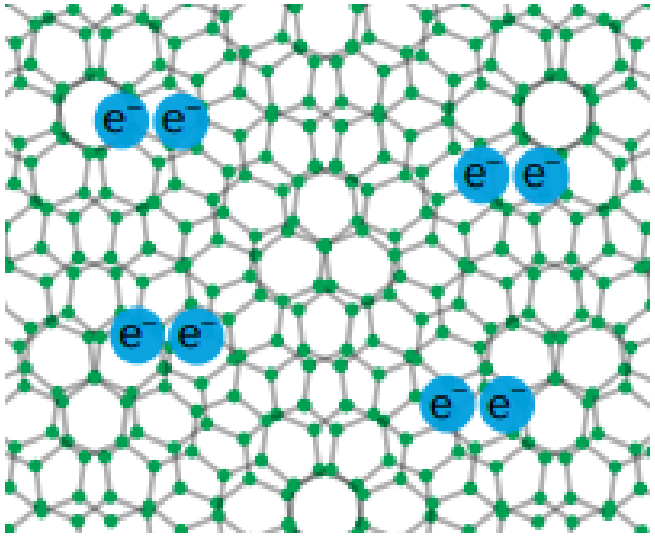
Kim et al., PNAS, 114, (2017)

Cheng et al., Chin. Phys. B, 28, (2019)

Weston et al., Nature Nanotechn., 15, (2020)

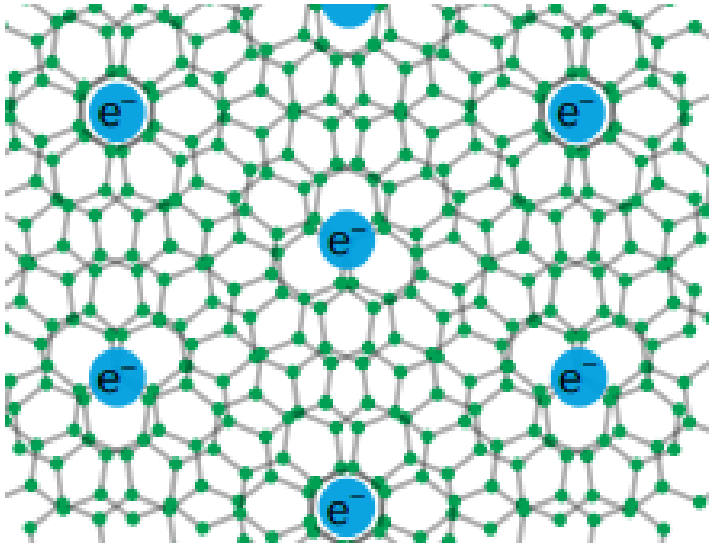
Properties of Moiré patterns

Superconductivity



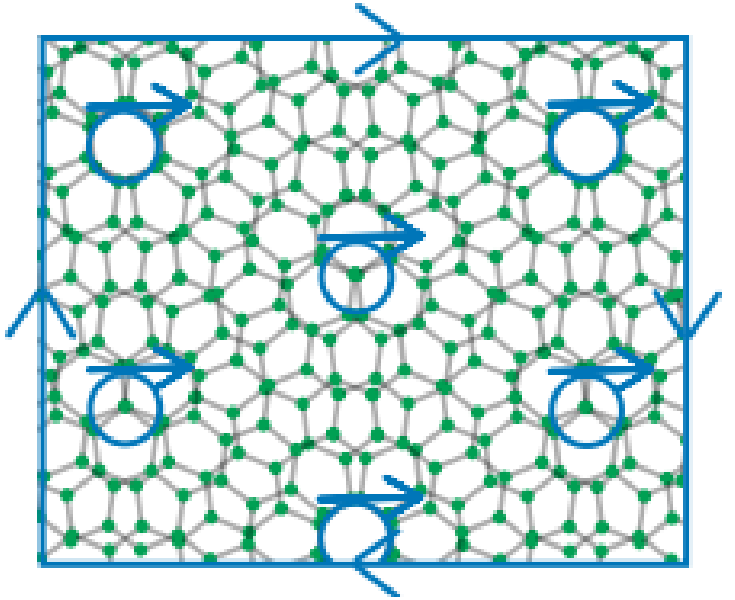
Transition temperature dependent on θ.

Mott insulator states



Highly localized states (whose density depends on θ).

Orbital magnetism



Moirè structuring of local magnetic moments

E.Y.Andrei et al., Nature Reviews, 2, (2021)

How to tune the 2D properties?

DOPING

Substitutional doping
Charge Trasfer
Intercalation
Electrostatic doping

PASSIVATION

Defect passivation

Surface encapsulation

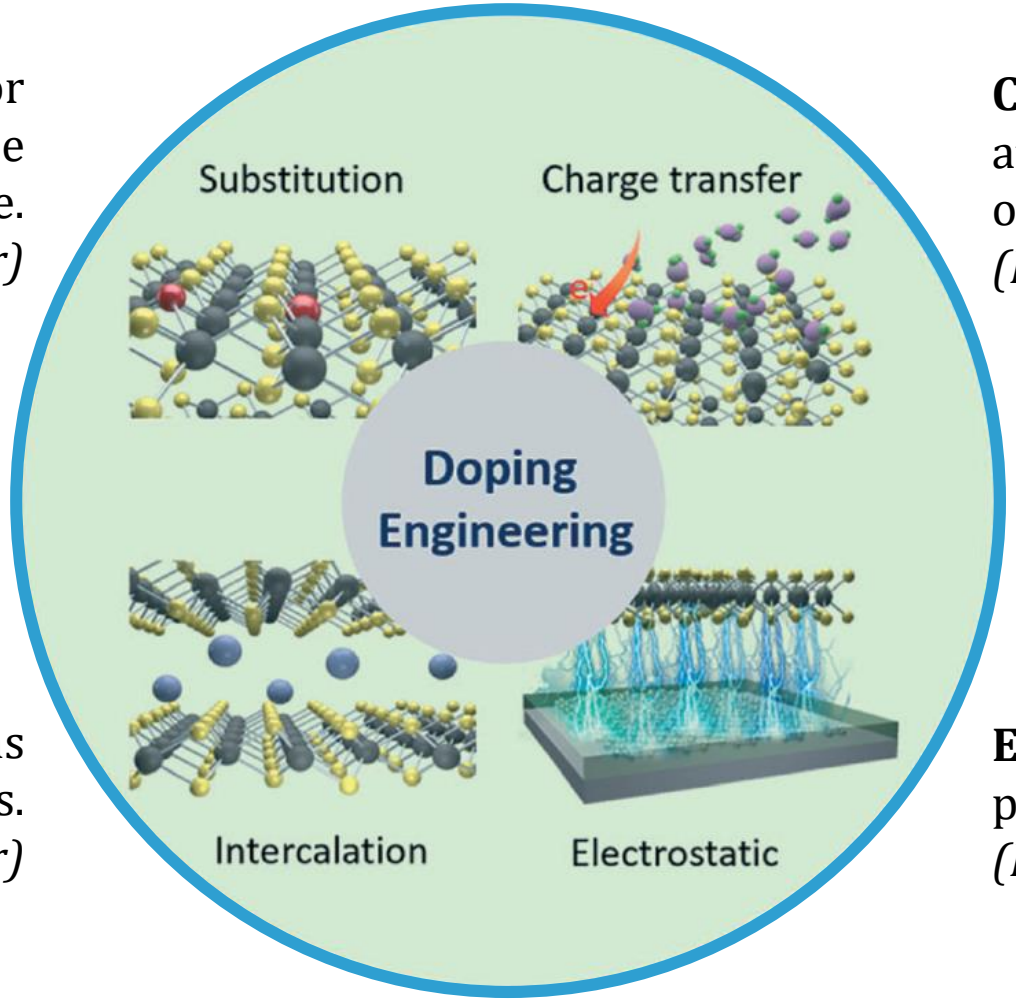
HETEROSTRUCTURING

Defect passivation

Surface encapsulation

Doping Strategies

Substitution of metal or chalcogen atoms in the lattice.
(Monolayer/Multilayer)



Charge transfer from atoms/molecules adsorbed on the surface to the layer.
(Monolayer)

Intercalation of atoms between crystal layers.
(Multilayer)

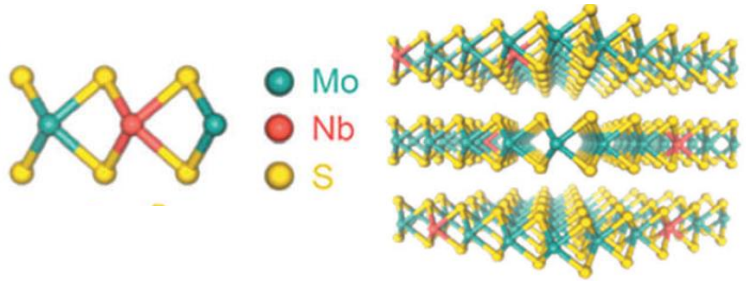
Electrostatic charge pumping.*
(Mono-, Bi-Layer)

Balasubramaniam et al., Mol. Syst. Des., 4, (2019)

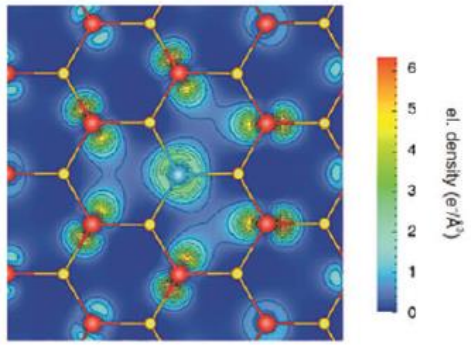
** Following the Grundmann definition (*Doping is … "The modification of the conductivity of a semiconductor using point defects"*), this is not doping. This phenomenon occurs also in bulk and thin films semiconductors but its effect can be persistent in VdW materials.*

Substitutional Doping (1)

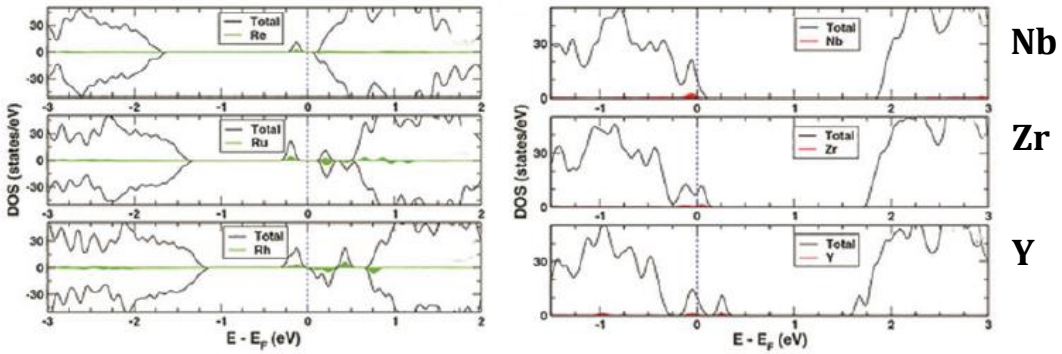
Substitution of metal atoms in the lattice (Mo, W → T)



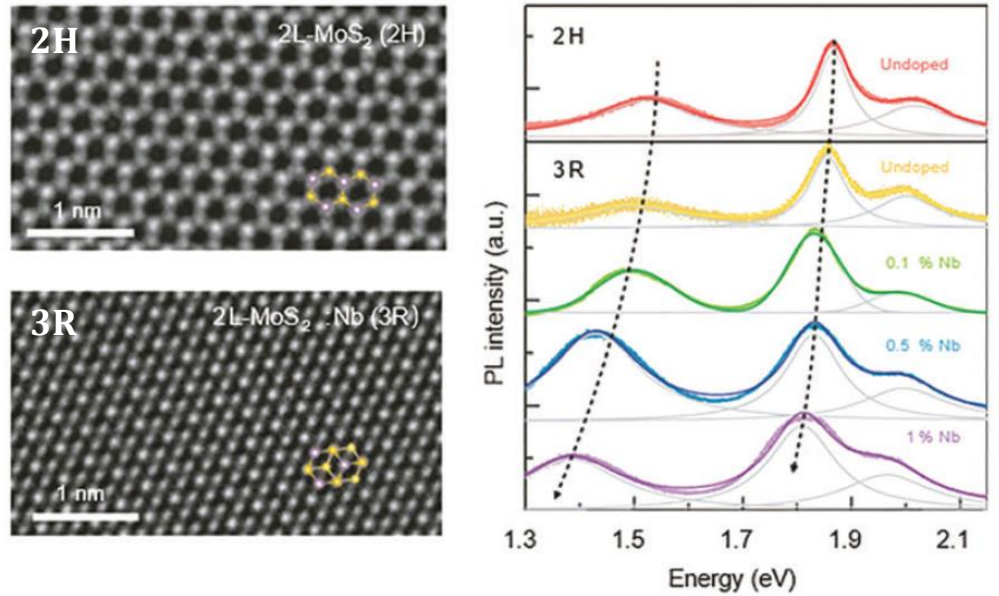
Electron density in Nb:MoS_2



Electronic density of states of T:MoS_2

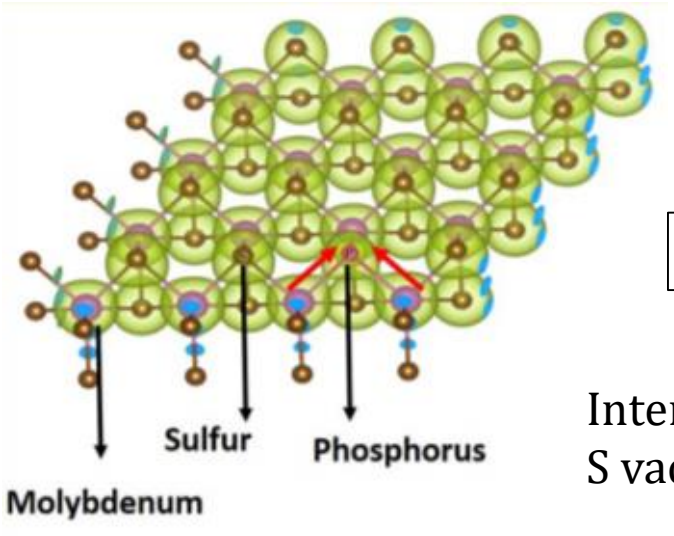


Luo et al., Nanoscale Horiz., 4, (2019)



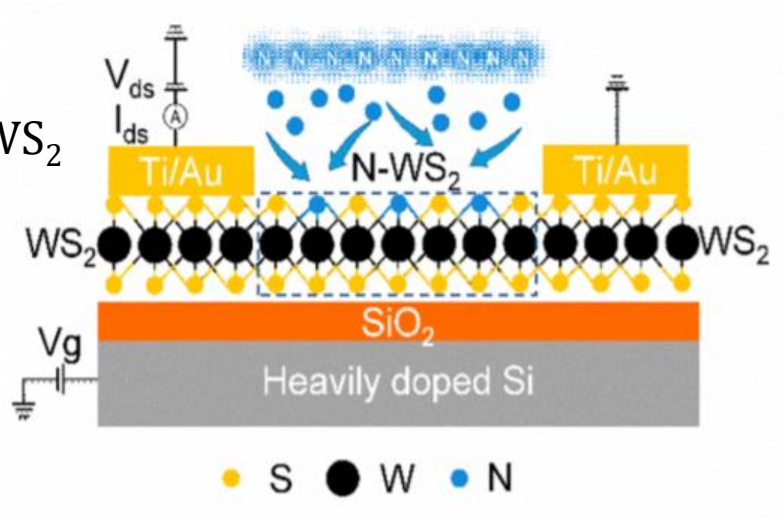
Due to the layered nature, metal substitutional doping may induce a phase transition.

Substitutional Doping (2)



Ion implantation of P and N

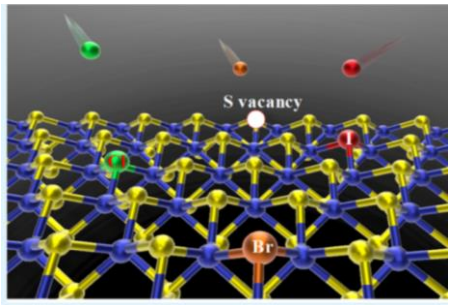
Substitutional N in WS_2



p-dopants

Interstitial P in MoS_2
S vacancy enhancement

Halide assisted Growth



n-dopants

Cl, Br, I in S vacancy sites
Passivation effect

Nipane et al., ACS Nano, 10, (2016)
Tang et al. ACS Nano, 12, (2018)
Wang et al., ACS Appl. Mater. Interfaces, 12, (2020)

Substitutional doping resuming table

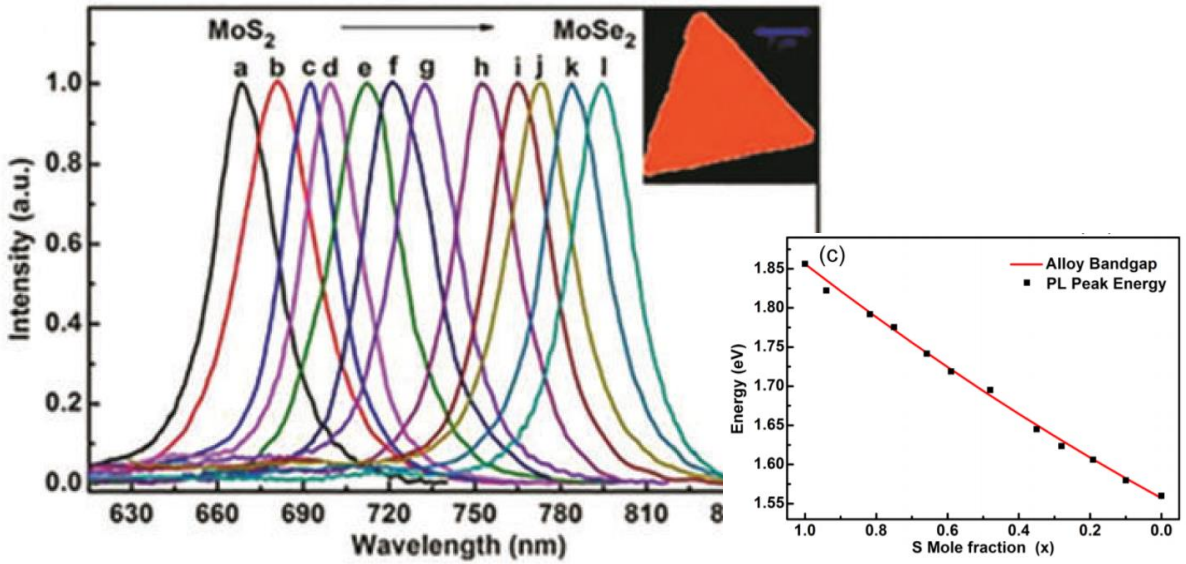
MX_n	Dopant	Type	Concentration [cm^{-2}]	Mobility [$cm^2\ V^{-1}\ s^{-1}$]	Ref.
MoS_2	Nb	p	1.8×10^{14}	14	32
	P	p	10^{10}–10^{12}	137.7	33
	Re	n	5.5×10^{12}	—	80
$MoSe_2$	W	p	4.0×10^{11}	1.6	86
WS_2	N	p	3.83×10^{11}	1.7	87
	Cl	n	6.0×10^{11}	60	88
WSe_2	S	n	—	68.2	89

2D Alloys

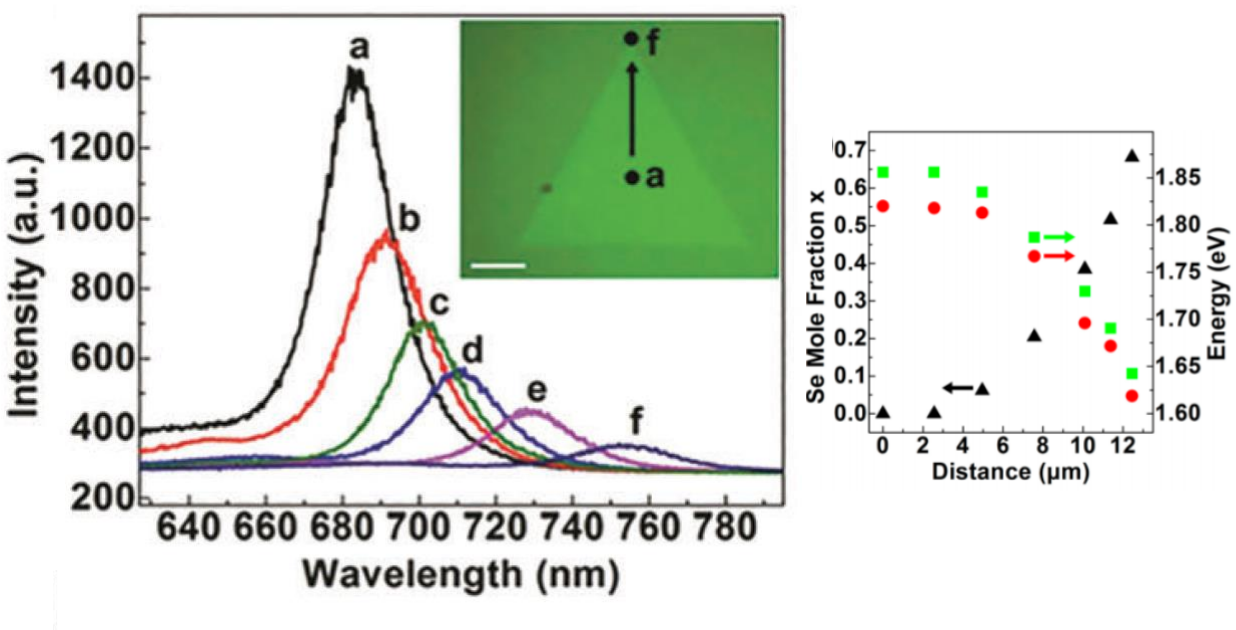
~~Alloying ~ Isoelectronic doping~~

Metal and chalcogen alloying induces a modification of the conduction or valence band, directly impacting the band gap and the functional properties.

PL spectra of homogeneous $MoS_{2x}Se_{2(1-x)}$



PL spectra of gradient $MoS_{2x}Se_{2(1-x)}$

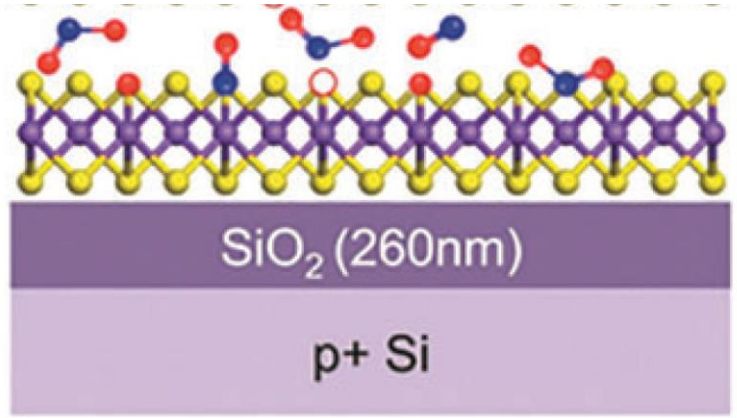


Luo et al., Nanoscale Horiz., 4, (2019)

Charge Transfer Doping (1)

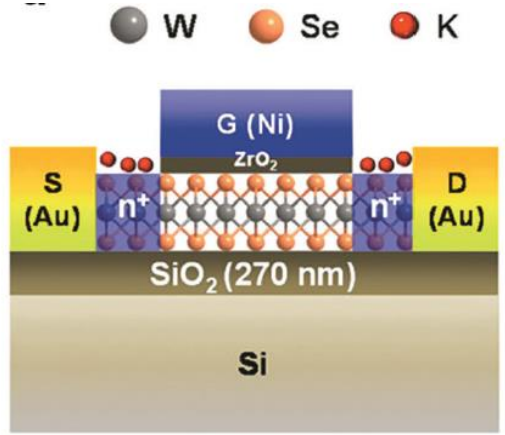
Doping occurs through charge transfer from/to species with different chemical nature which are not chemically bonded with the atomic layer

Gaseous molecules can adsorb on the surface and induce charge transfer (adatom dopants).



TBN: Adsorption occurs on preferntial sites such as grain boundaries or vacancies.

Metal atoms provide electrons/holes to the layer depending on the relative work functions.



Luo et al., Nanoscale Horiz., 4, (2019)

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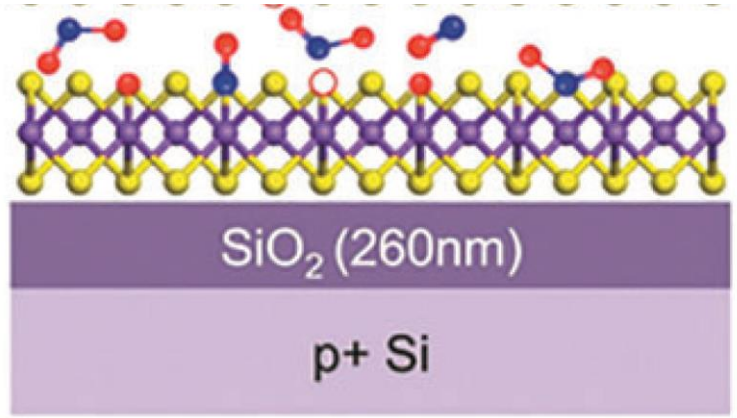

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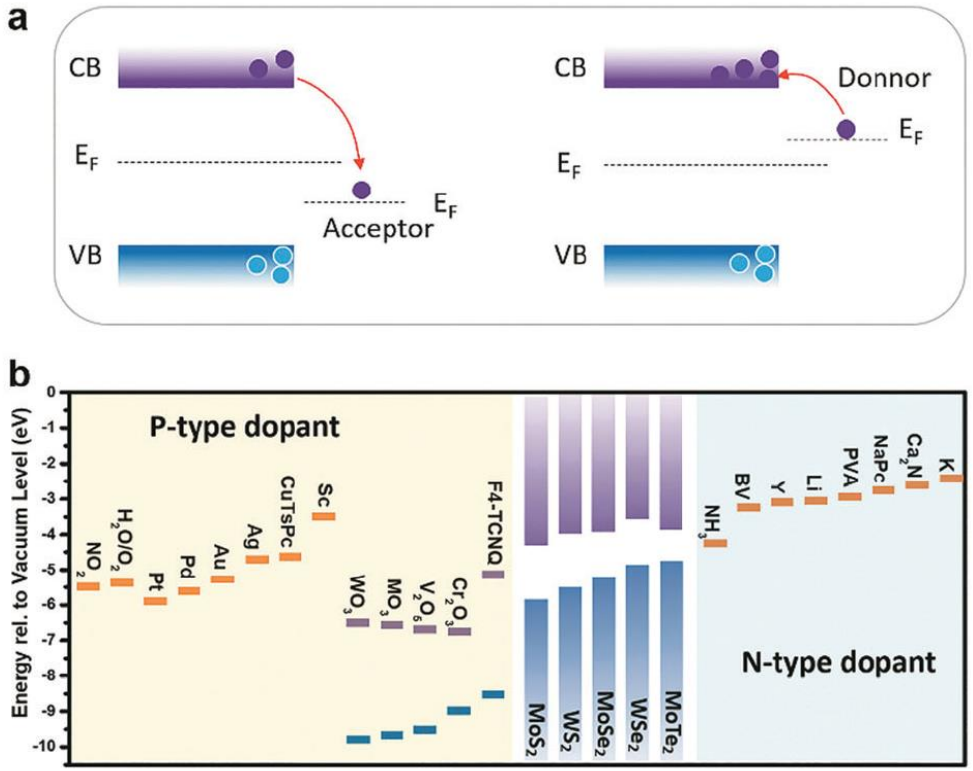
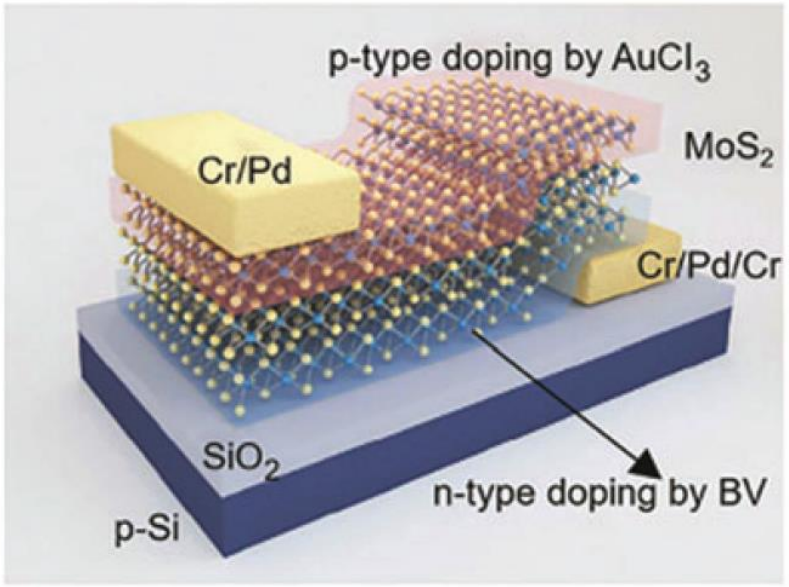


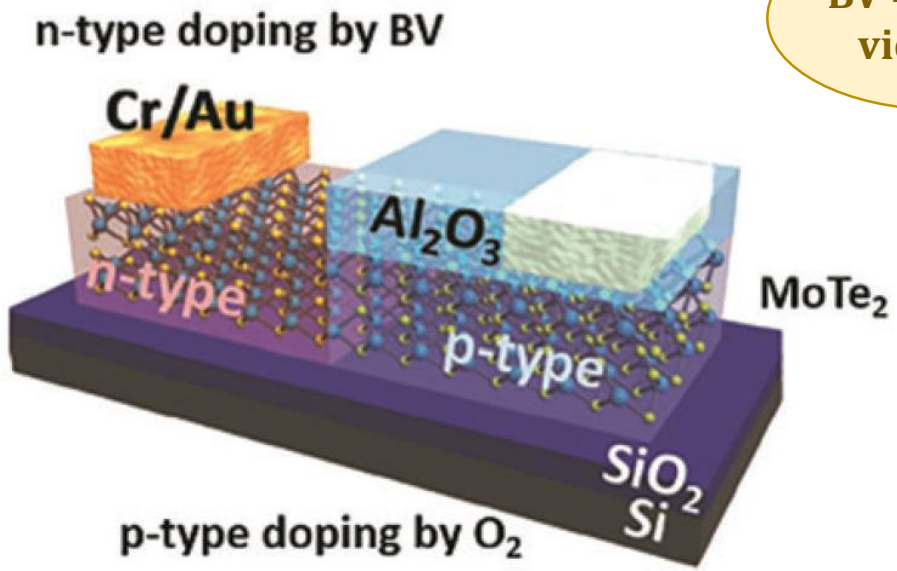
Luo et al., Nanoscale Horiz., 4, (2019)

Charge Transfer Doping (2)

Vertical p-n junction



Lateral (Horizontal) p-n junction



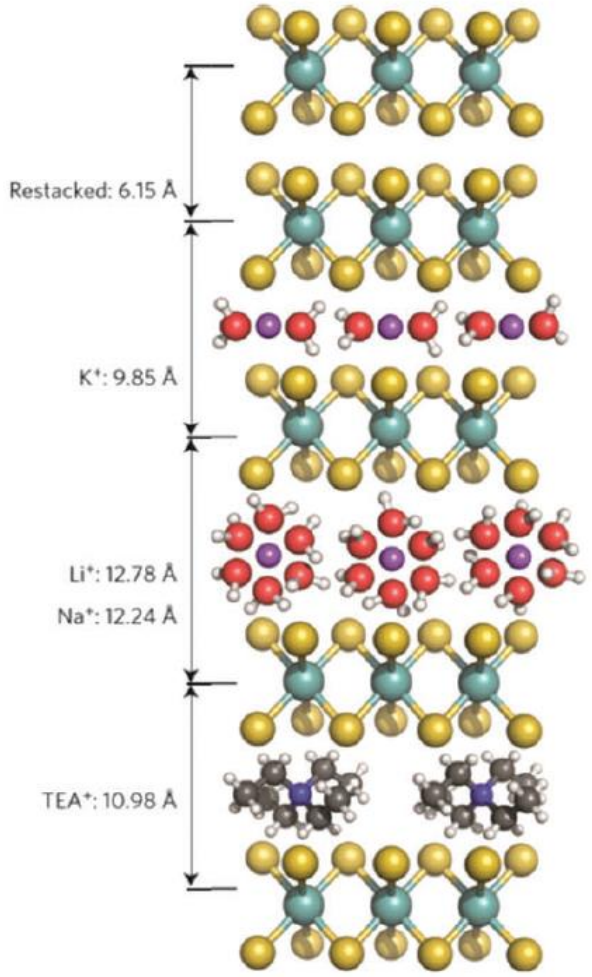
BV = Benzyl viologen

Charge transfer allows to dope the material after the synthesis (less impact on the atom arrangement) and it is convenient to engineer selected areas of interest.

Luo et al., Nanoscale Horiz., 4, (2019)

Intercalation Doping

Example of intercalation doping in MoS_2



Intercalation is able to modulate the crystal lattice and electronic structure of host materials, as well as providing charges (depending on the donor/acceptor nature of the foreign atoms).

The larger the size of the foreign impurity, the larger the distortion of the crystal and thus the effect on the electronic structure.

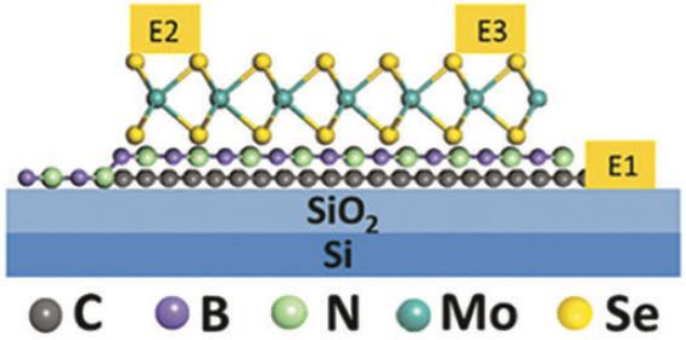
Typical intercalation doping is obtain through:

- *Hydrogen*
- *Alkali Metals (Li, Na, K)*
- *Heavy Metals (Cu, Co)*
- *Organic compounds (Triethylamine)*

Increasing atomic/molecular size

Luo et al., Nanoscale Horiz., 4, (2019)

Electrostatic Doping



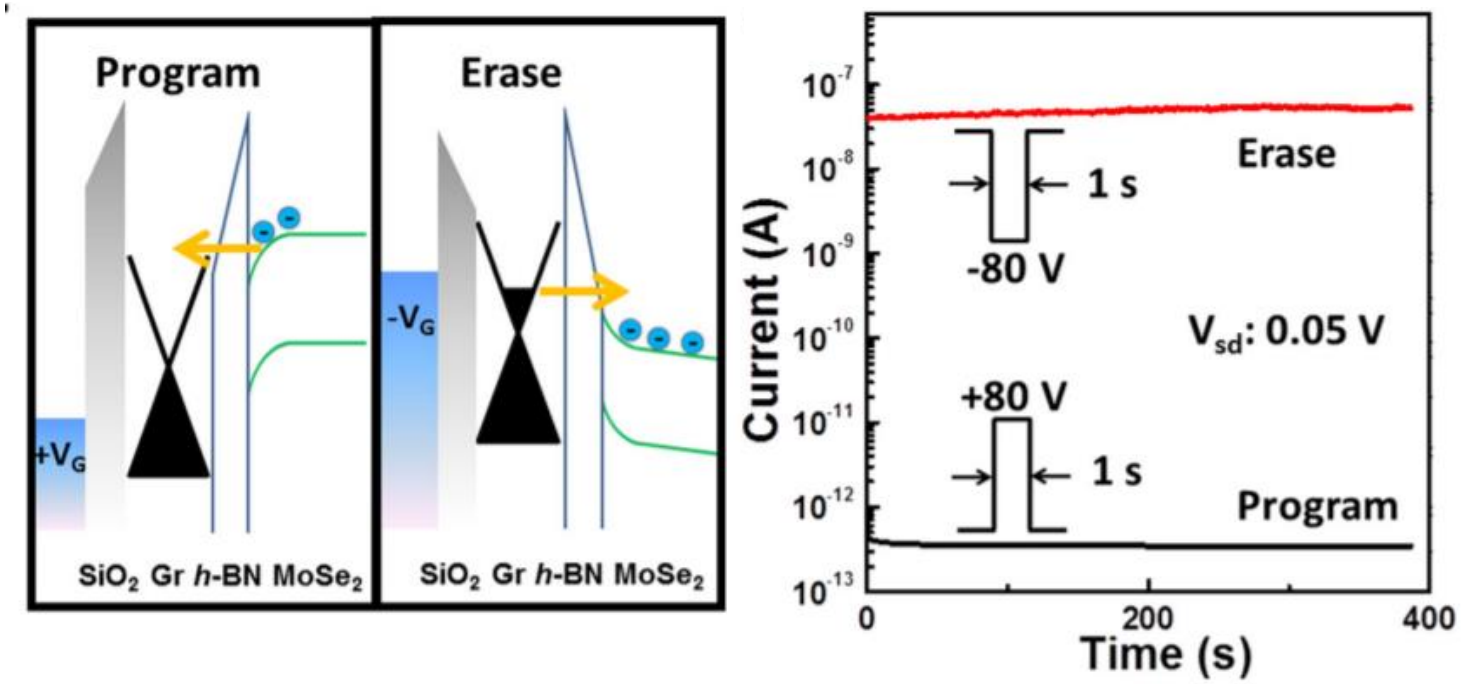
Gate-controlled potential difference can induce carrier injection into semiconductors.

Usually this phenomenon is NOT considered doping!

Due to their atomic thickness, TMDs are highly sensitive to electric field and thus some method can ensure a doping-like effect even after withdrawal of the gate bias.

Luo et al., Nanoscale Horiz., 4, (2019)

Floating Gate Modulation



Electrons tunnel in from the graphene contact through the h-BN (the direction depends on the applied gate bias, here named «Erase» and «Program»).
By applying a high Vg for a short time (1s), the channel conductivity changes for a long time.

Cheng et al., Appl. Phys. Lett. 110, (2017)