Self-consistent perturbation theory for two dimensional twisted bilayers

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Coupled Mathematical Models for Physical and Biological Nanoscale Systems and Their Applications, BIRS- Banff, Canada

Perturbation theory for weakly coupled two-dimensional layers, Journal of Materials Research, 31 (07), 959-966 (2016).

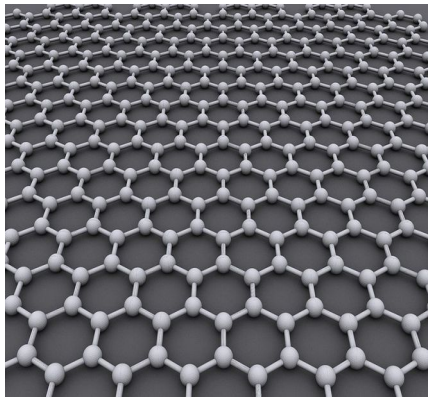
2D materials

- Class of materials merely a few atoms thick
- Exhibit exotic/novel properties

} Applications in solar cells, transistors, semiconductors

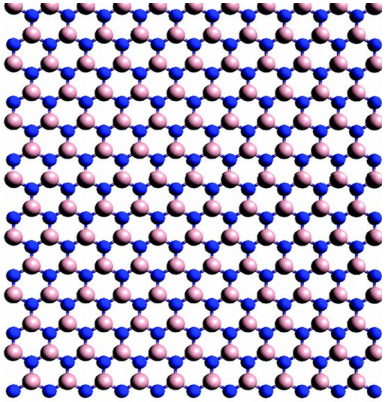
Graphene Family

Graphene



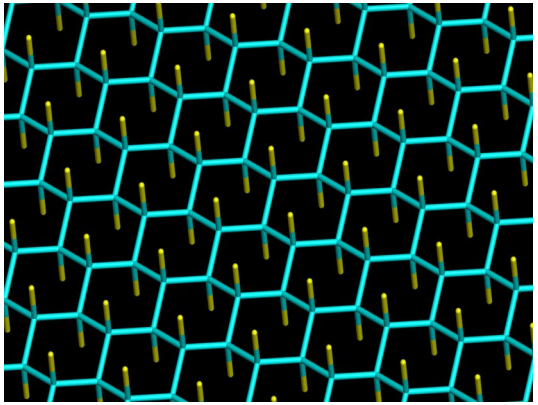
sp2 hybridized single atom thick C sheet

Hexagonal boron-nitride



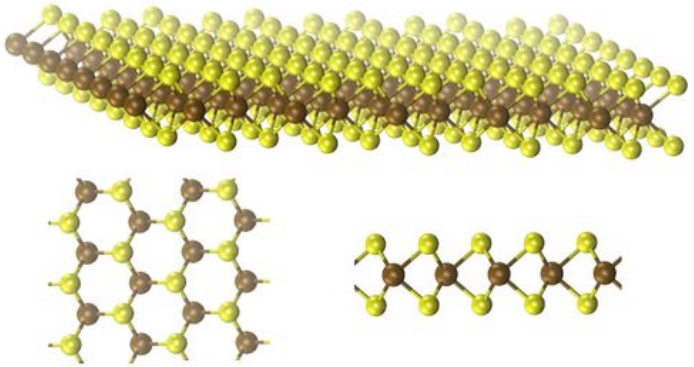
sp2 hybridized B-N in graphene structure

Fluorographene



Fluorine saturated graphene

Transition metal dichalcogenides family

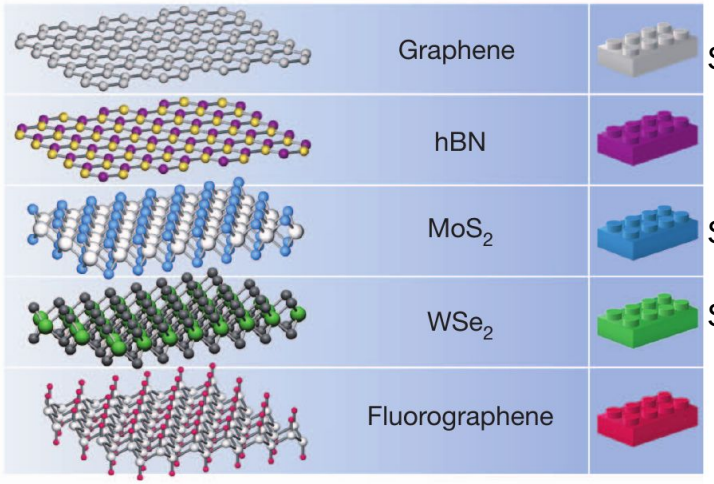


MoS_2, WS_2, $MoSe_2$, WSe_2 : 3 atomic layers thick

Except graphene, all above materials are semiconducting/insulating

Layered structures

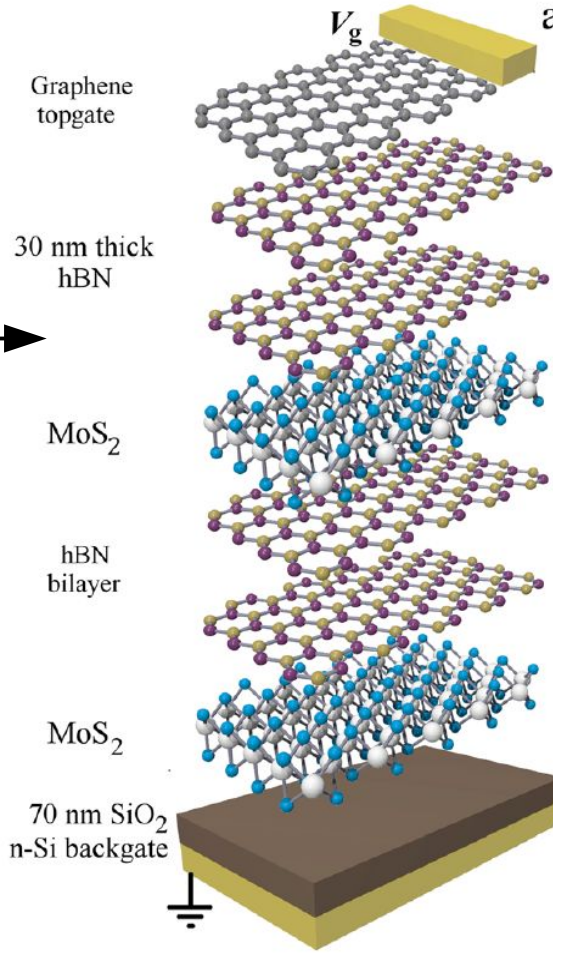
A. K. Geim (doi:10.1038/nature12385)



Semi-metal
insulator
Semi-conductor
Semi-conductor
insulator

2D layers
as Lego blocks

Build designer
heterostructures
by stacking



Calman *et. al.* APL 108, 101901 (2016)

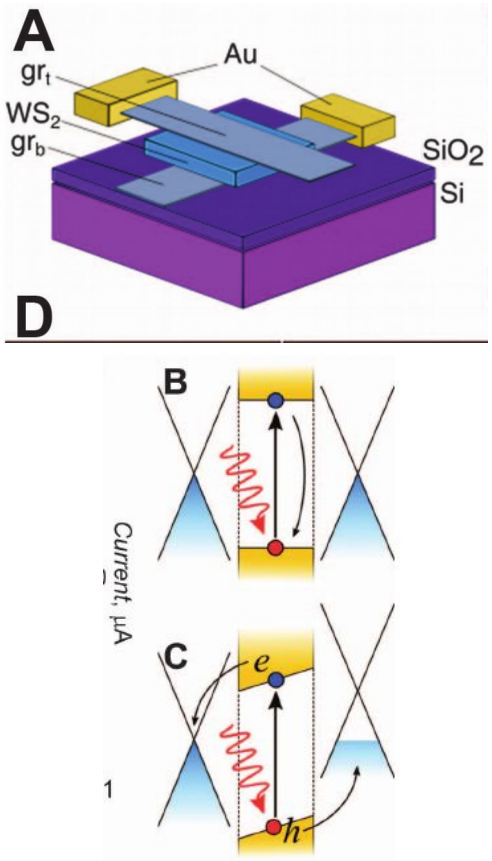
weak interplanar bonding: van der Waals heterostructures

- Clean and atomically sharp interfaces
- Lattice mismatch
- Rotations between layers
- Stacking order

Unusual properties and new phenomena can be explored!

Applications and interesting phenomena

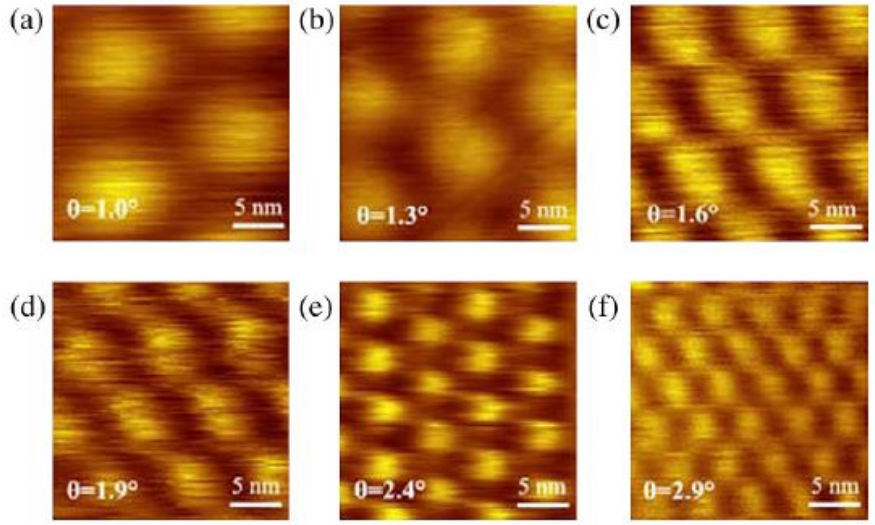
Excitons: Photovoltaic device



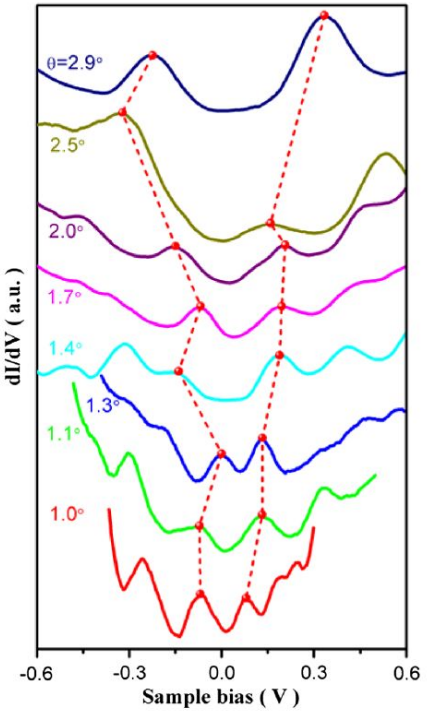
L. Britnell *et al* (K. S. Novoselov), Science 340, 1311 (2013)

- Ultra-thin and flexible
- 30% quantum efficiency

Moire patterns: rotated layers



Yan *et. al.* PRL 109, 126801 (2012)



Bilayer graphene

- Fermi velocity renormalization
- Van Hove singularities
- Commensurate to incommensurate transition

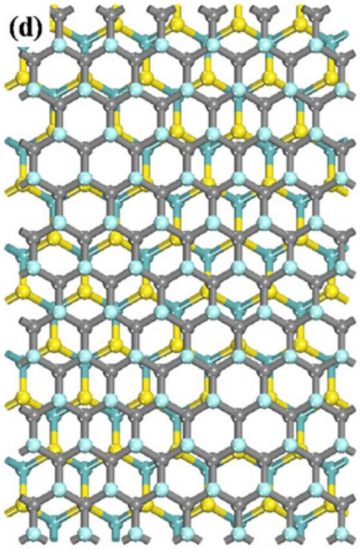
Different structures due to layering

- Stacking sequences between layers: AA, AB, ABC, …
- Incommensurate layers

$$\frac{a1}{a2} = \begin{cases} \text{Commensurate} & \text{: rational number} \\ \text{Incommensurate} & \text{: irrational number} \end{cases}$$

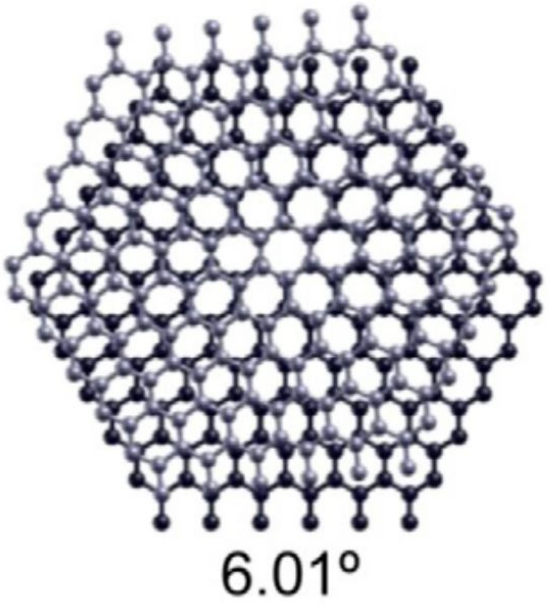
Rotation of layers

Fluorographene
-MoS_2 bilayer



Lin-Feng Wang *et al*, Nanotechnology 25, 385701 (2014)

bilayer
graphene

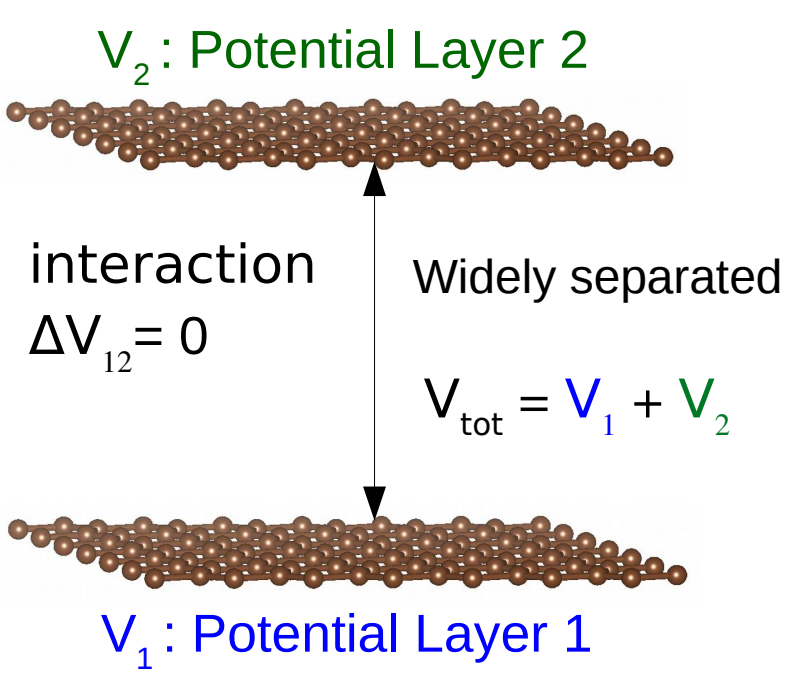


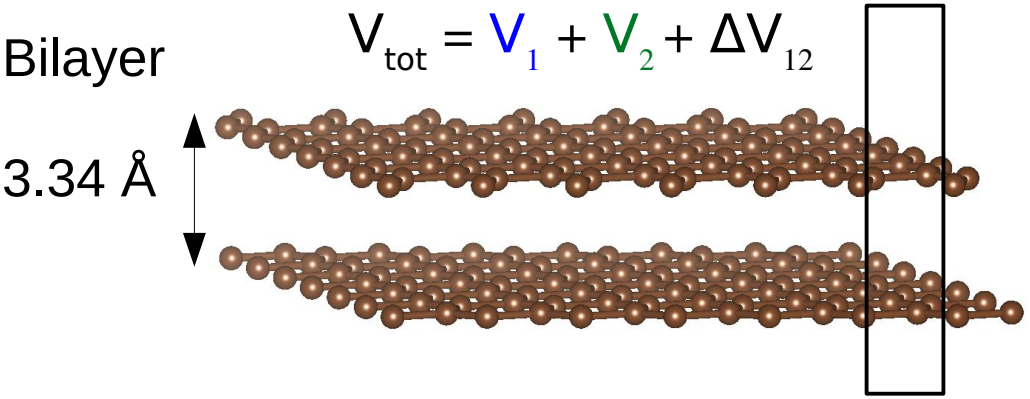
T G Mendes-de-Sa *et al,* Nanotechnology 23, 475602 (2012)

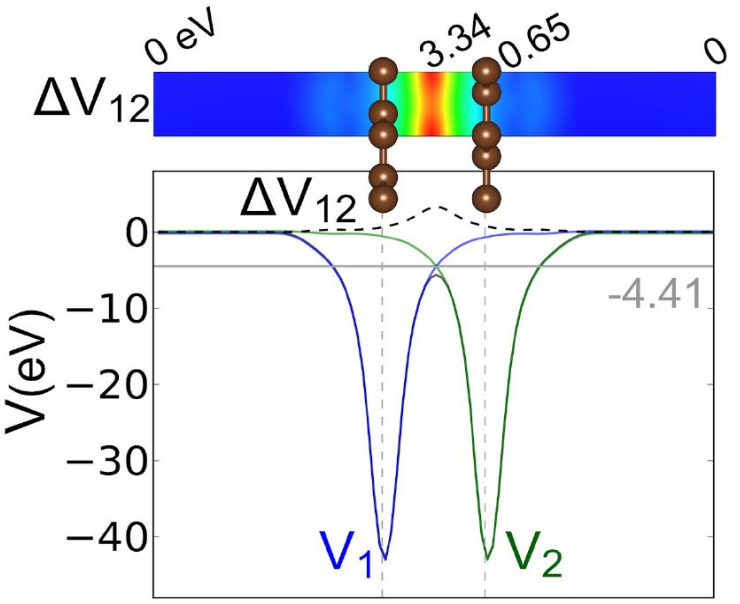
DFT simulations of incommensurate/rotated layers need large and expensive supercell calcs.

Can we circumvent full DFT calculations?

What in DFT calcs. is expensive?







- ΔV_{12} required to get exact solution
  - → Needs full DFT calcs.
  - → Expensive for incommensurate / rotated structures
- Weakly interacting layers: Apply perturbation theory!
  - Approximate / self-consistently determine ΔV_{12}
  - $V_2 + \Delta V_{12}$ acts as perturbation on layer 1 & vice versa

No full DFT calcs. on supercell!

Model

- Holds for finite systems (commensurate/incommensurate)
- Wavefunction total system = Linear combination of individual layers

$$\psi_N^{(n)} = \sum_{m=1}^{N} c_{1,N}^{(n,m)} \psi_1^{(m)} + c_{2,N}^{(n,m)} \psi_2^{(m)},$$

- Solve the generalized eigenvalue problem

$$\mathcal{H}_N C_N^{(n)} = \epsilon_N^{(n)} S_N C_N^{(n)}.$$

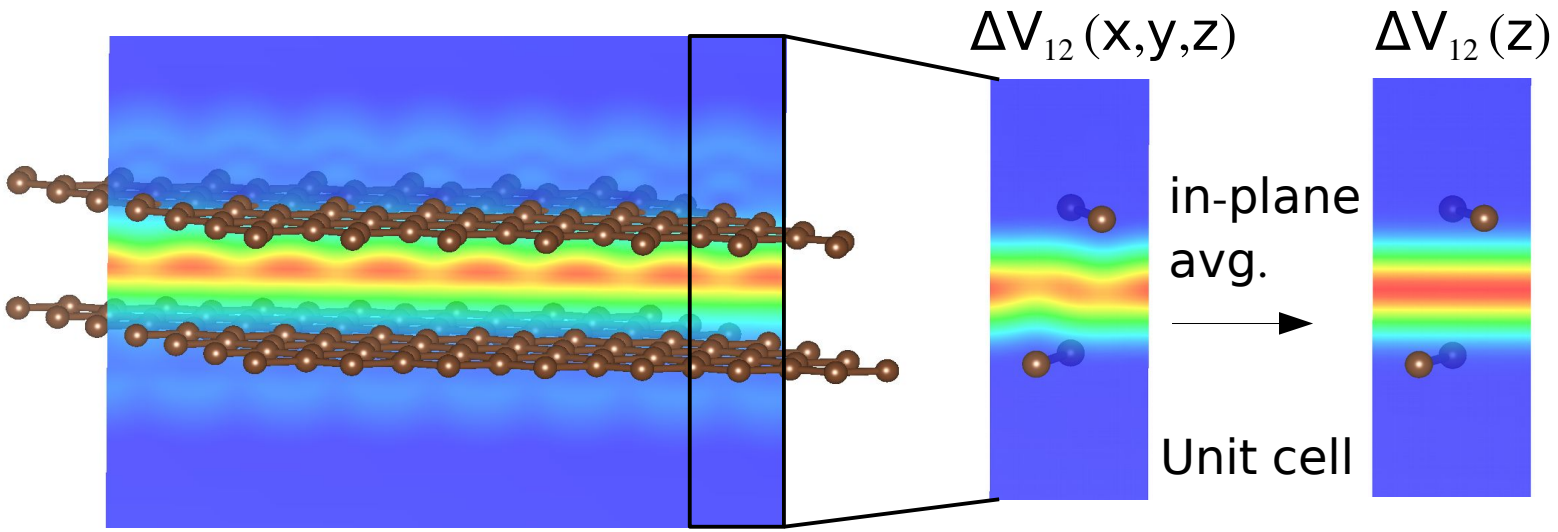
$$\mathcal{H}_N = \left[\begin{array}{c|c} H_{11}\ \text{(intralayer)} & H_{12}\ \text{interlayer} \\ \hline H_{12}\ \text{interlayer} & H_{22}\ \text{(intralayer)} \end{array}\right]$$

isolated layer (unit cell) DFT calcs. are performed

What is the form of ΔV_{12} ?

Methodology

1) ΔV_{12} : in-plane avg.

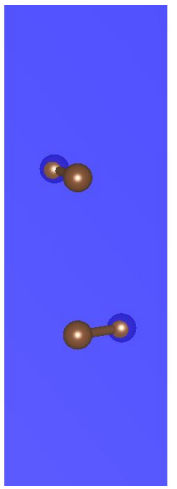


- $\Delta V_{12}(z)$: constant in x and y
- Extend $\Delta V_{12}(z)$ in-plane : rotated supercells
- Solve the eigenvalue problem once!

2) ΔV_{12} : self-consistent

- Begin with $\Delta V_{12} = 0$
- No approximations!

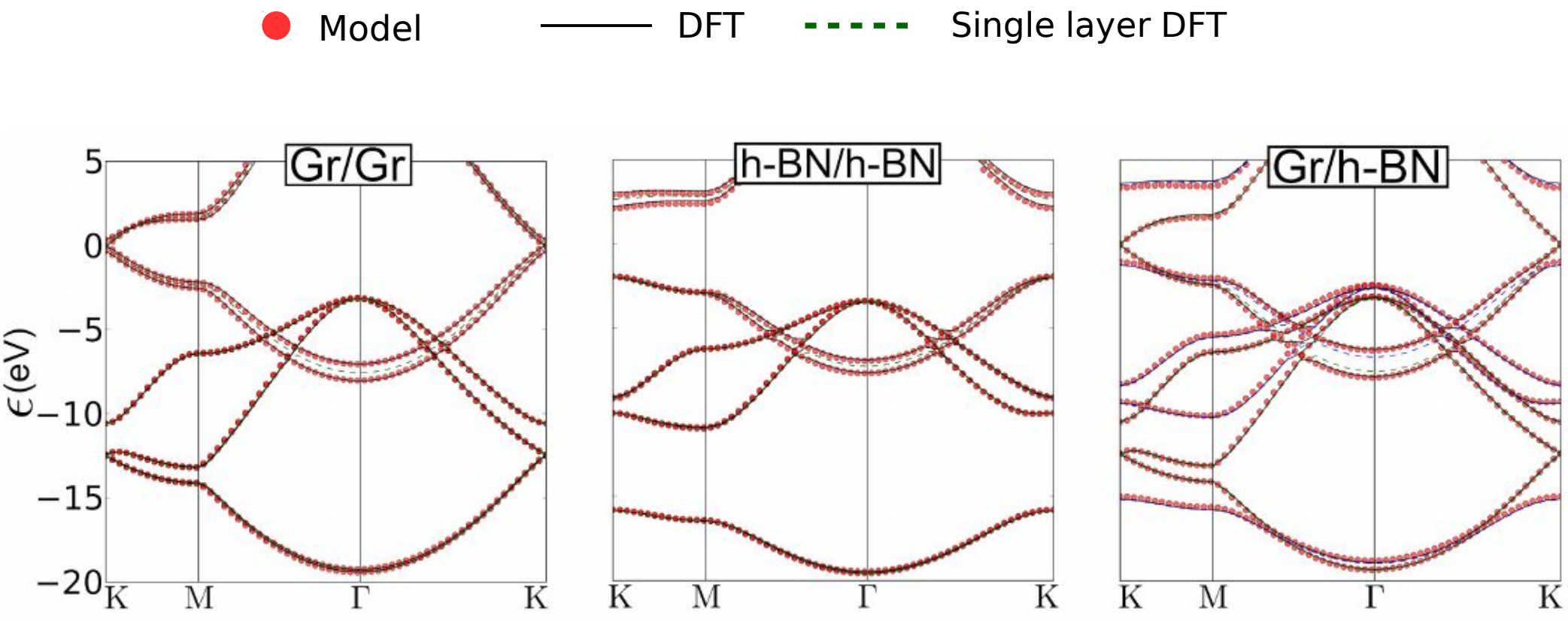
$\Delta V_{12} = 0$



Apply the model to periodic commensurate structures

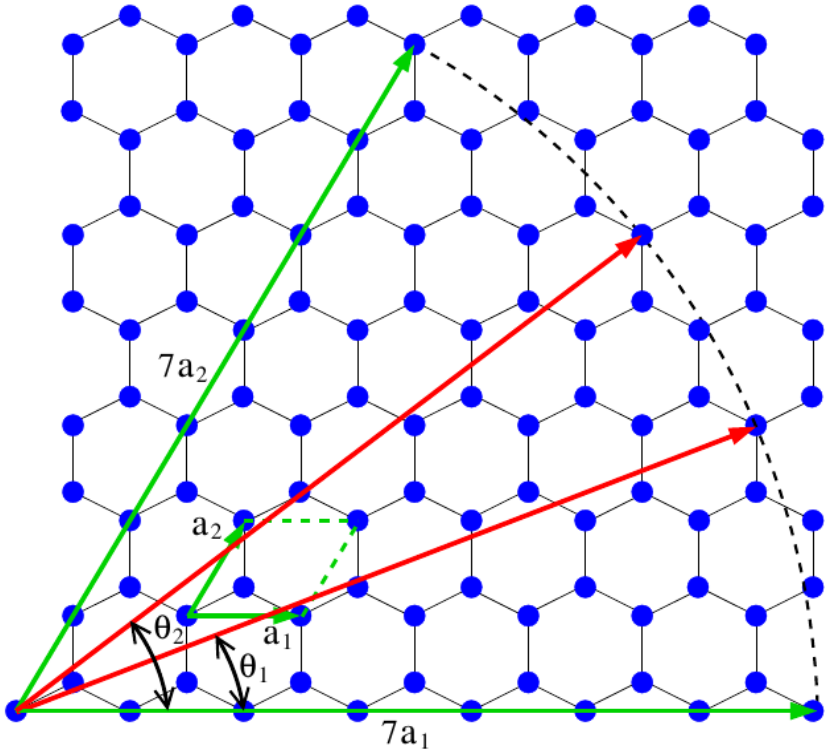
1) $\Delta V_{12}(z)$: in-plane averaged

- Unit cells (AB stacked)



Model results agree well with DFT results

Rotated structures



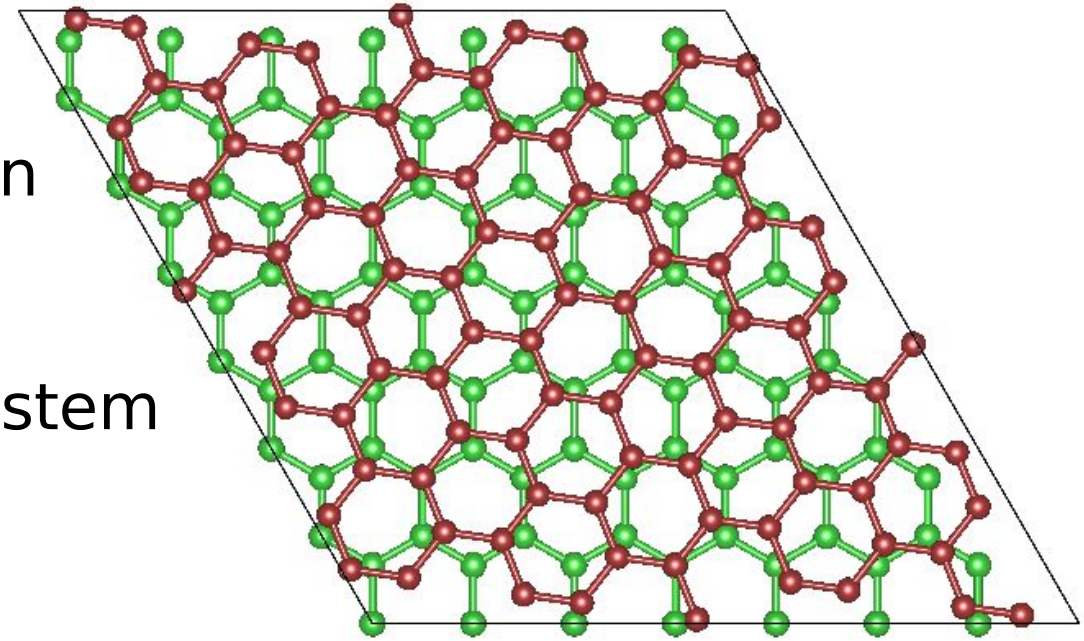
Rotated cell vector

Unrotated cell vector

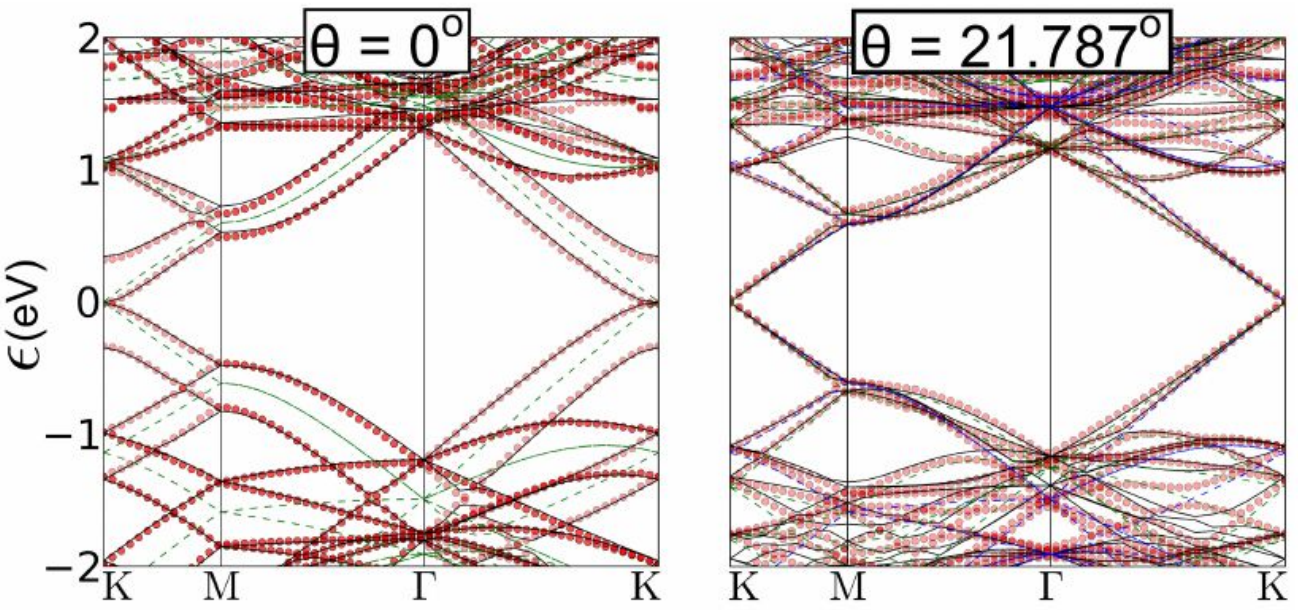
Form supercell with non-trivial rotations!

7x7 supercell: 21.787° rotation

We test our model on this system



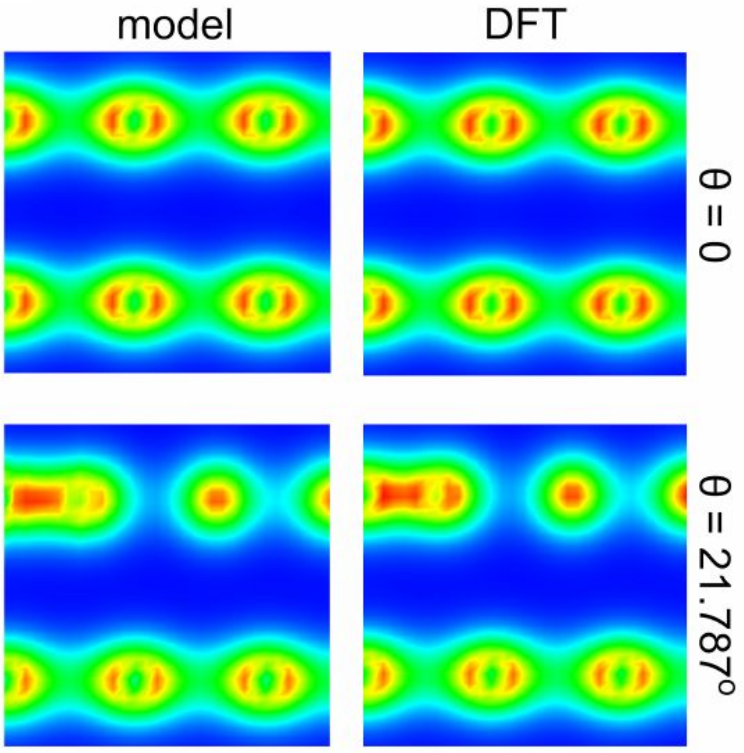
- Supercells: AB stacked Gr/Gr with and without rotation



7x7 supercell

Model — DFT - - - - Single layer DFT

Charge density



Max. Error ~ 0.05 eV for unrotated configurations!

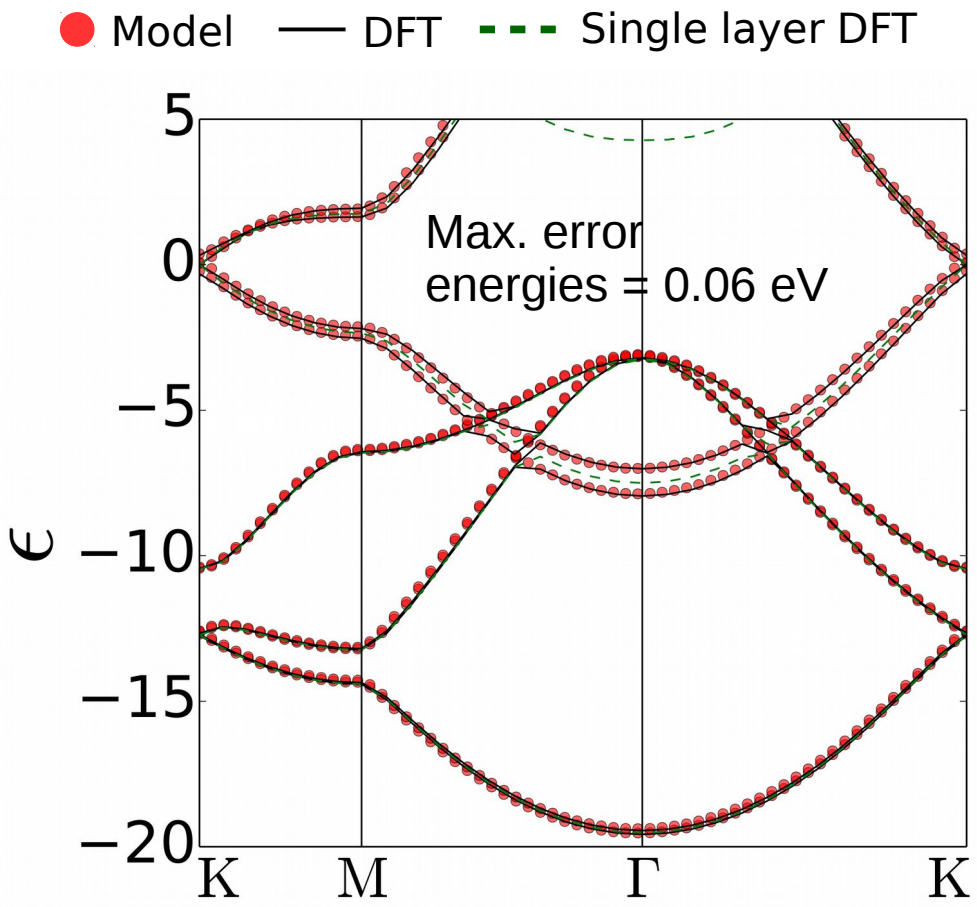
Model results agree well with DFT!

What happens in self-consistent determination of ΔV_{12}?

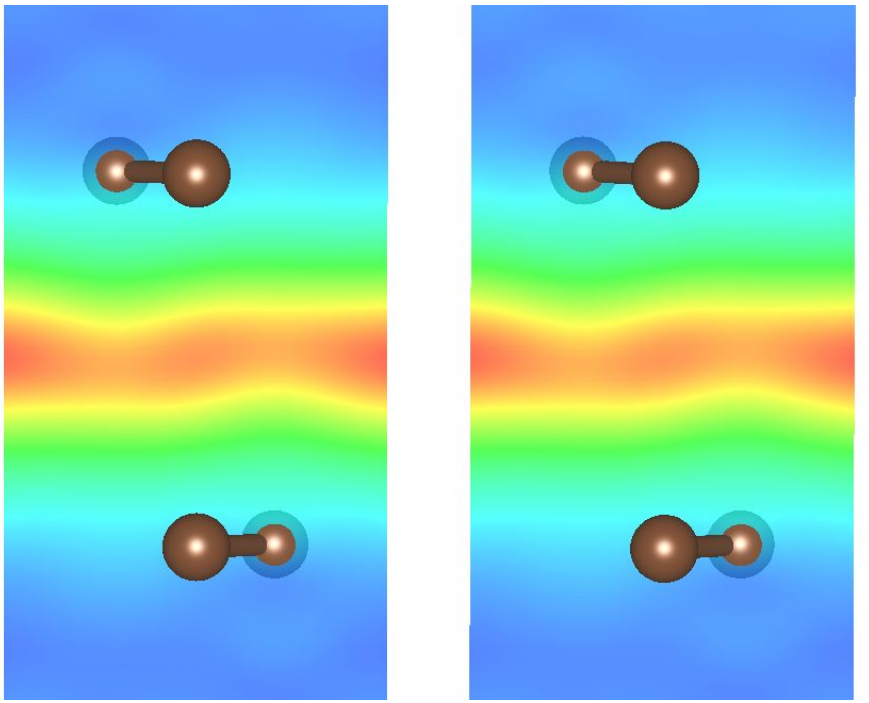
2) ΔV_{12}: Self-consistent

- Unit cells (AB stacked)

  a) Gr/Gr



ΔV_{12}

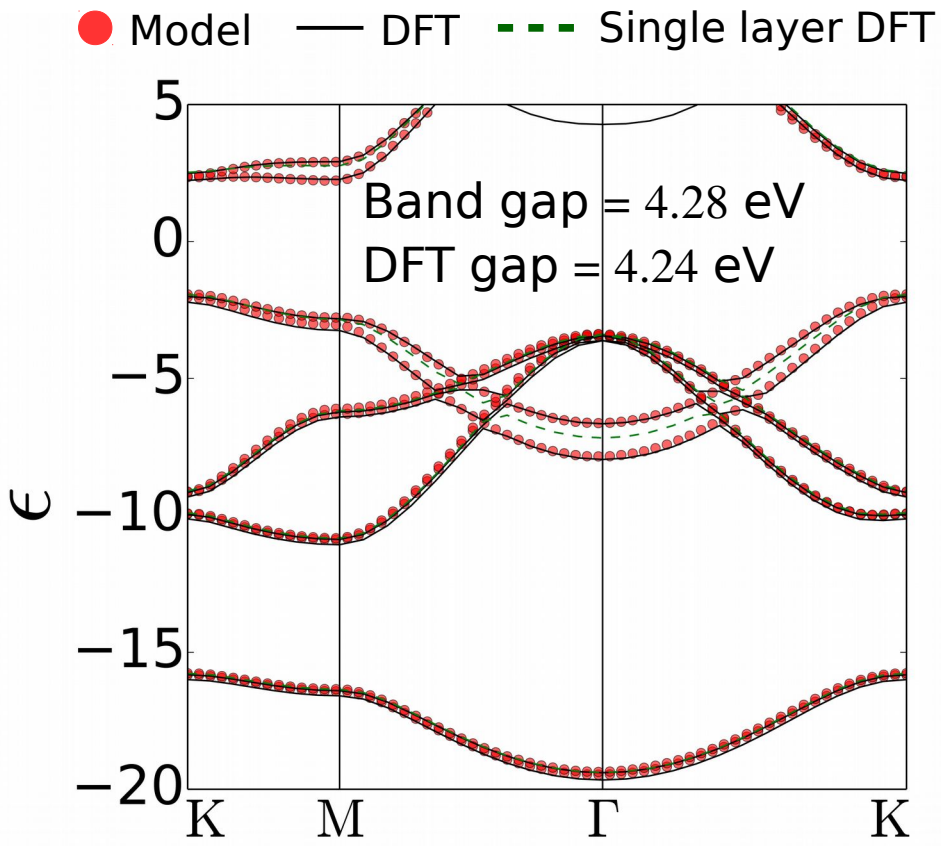


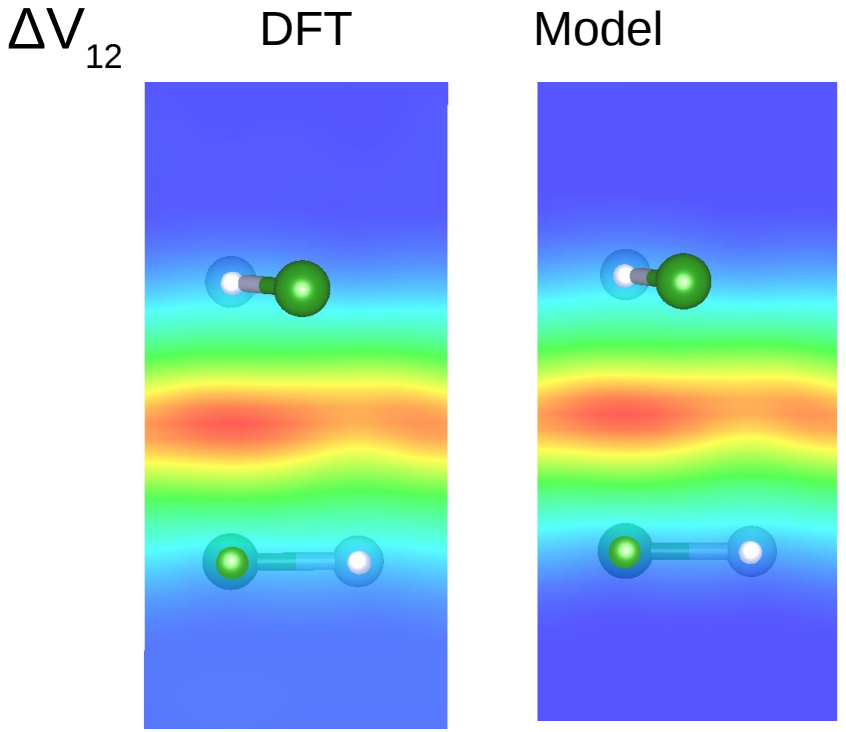
Energy	DFT	Model	Diff
Kinetic	572.69	572.05	-0.64
Hartree	-27.12	-27.26	-0.14
Exc	-38.34	-38.39	-0.05

Error varies linearly with iteration

Calculation converged at second step!

b) h-BN/h-BN



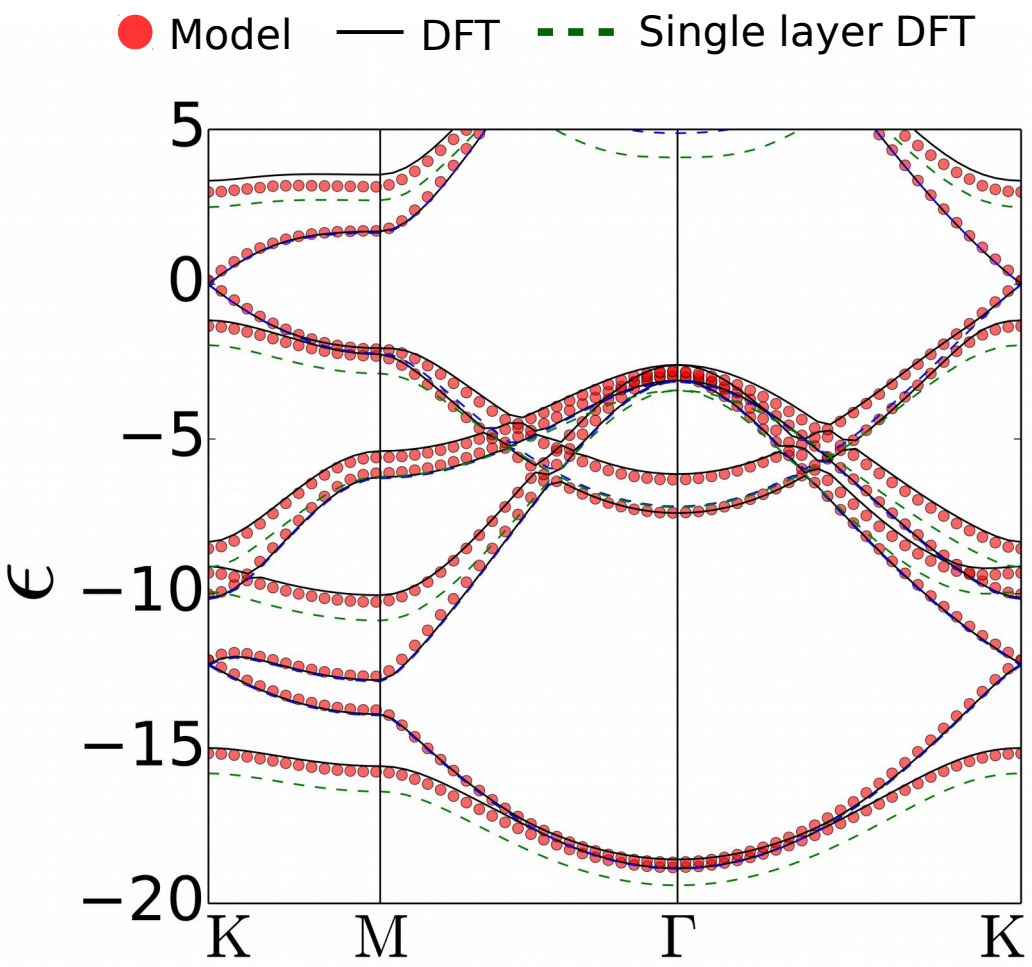


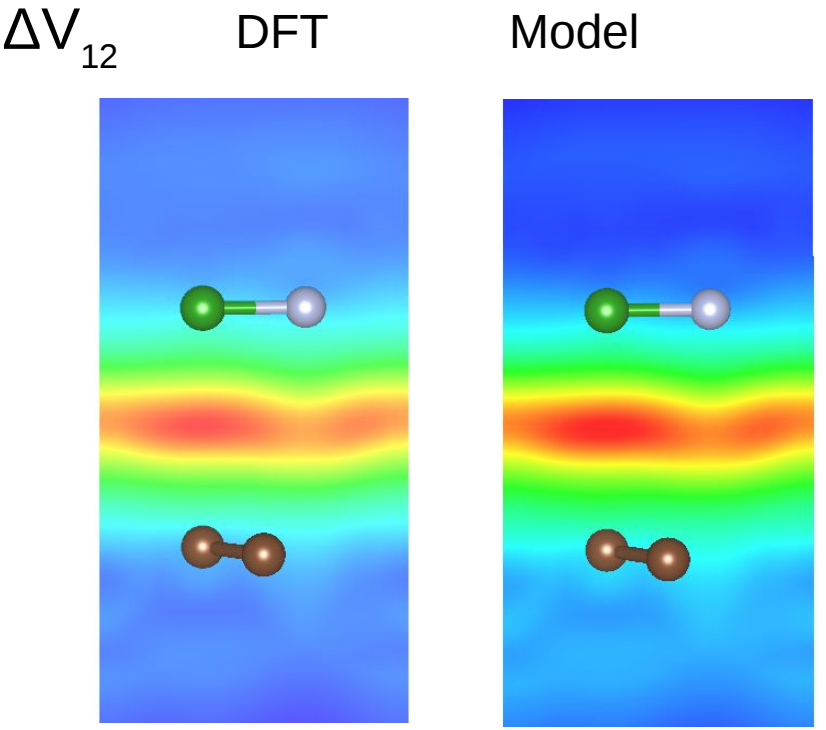
Energy	DFT	Model	Diff
Kinetic	643.37	642.86	-0.51
Hartree	-27.62	-27.64	-0.02
Exc	-37.04	-37.08	0.06

Error saturates at the first step.

Convergence is better for insulators!

c) Gr/h-BN



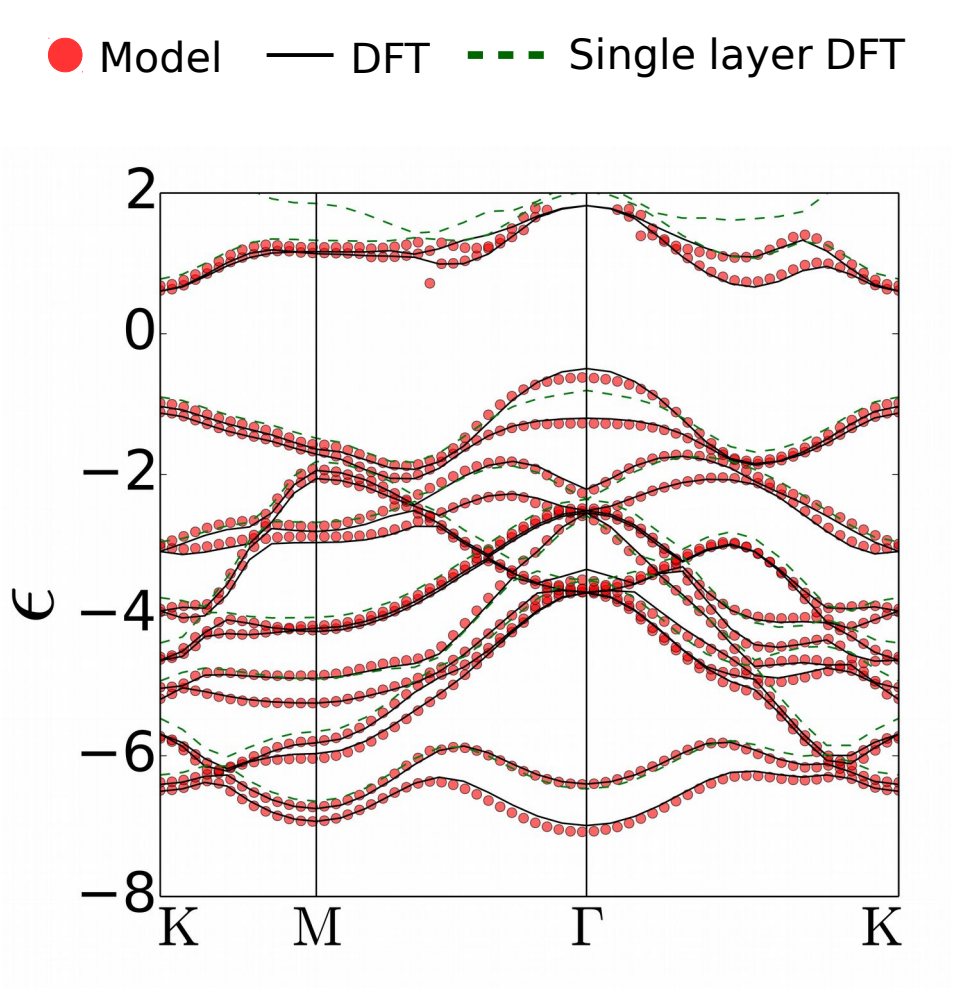


Band gap = 0.030 eV

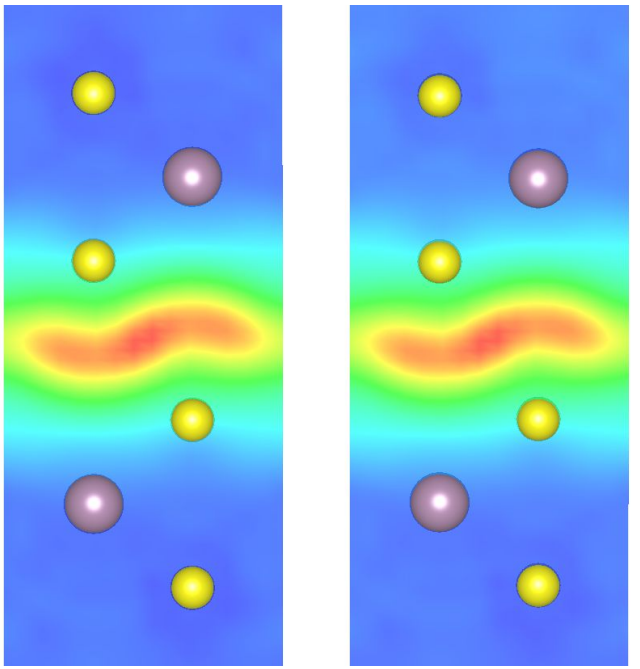
DFT gap = 0.038 eV

Energy	DFT	Model	Diff
Kinetic	605.24	604.58	-0.66
Hartree	-23.23	-23.38	-0.15
Exc	-36.45	-36.51	-0.06

d) MoS_2/ MoS_2



ΔV_{12} DFT Model

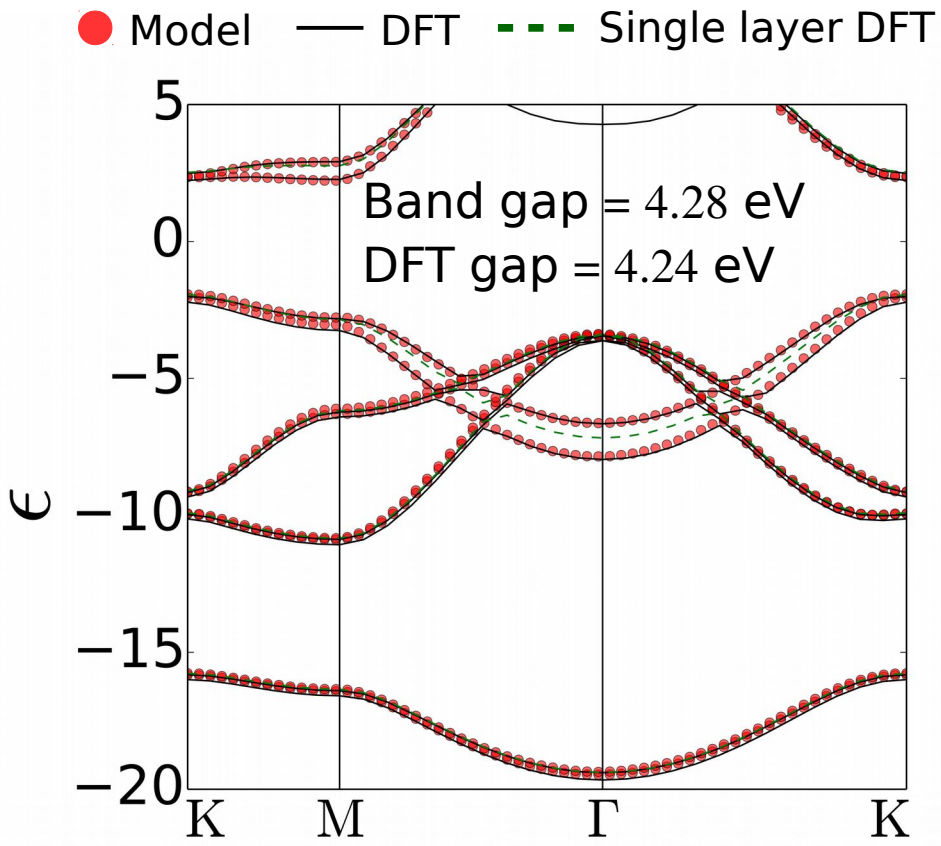


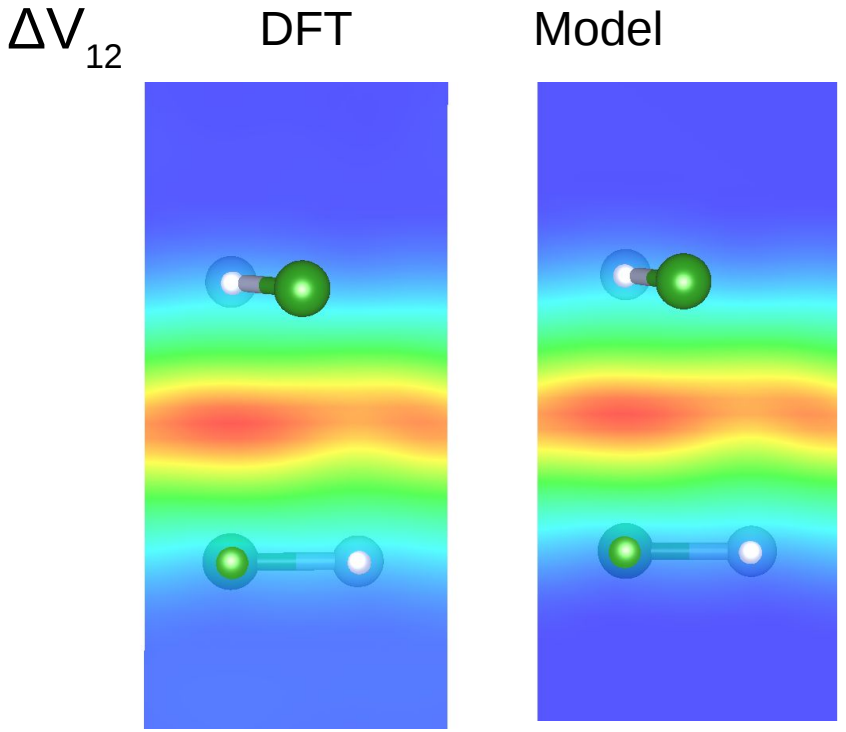
Energy	DFT	Model	Diff
Kinetic	1493.32	1491.40	-1.92
Hartree	-22.34	-22.81	-0.47
Exc	-35.99	-36.08	-0.09

Error larger than Gr-Gr.

The band structure is well represented!

b) h-BN/h-BN





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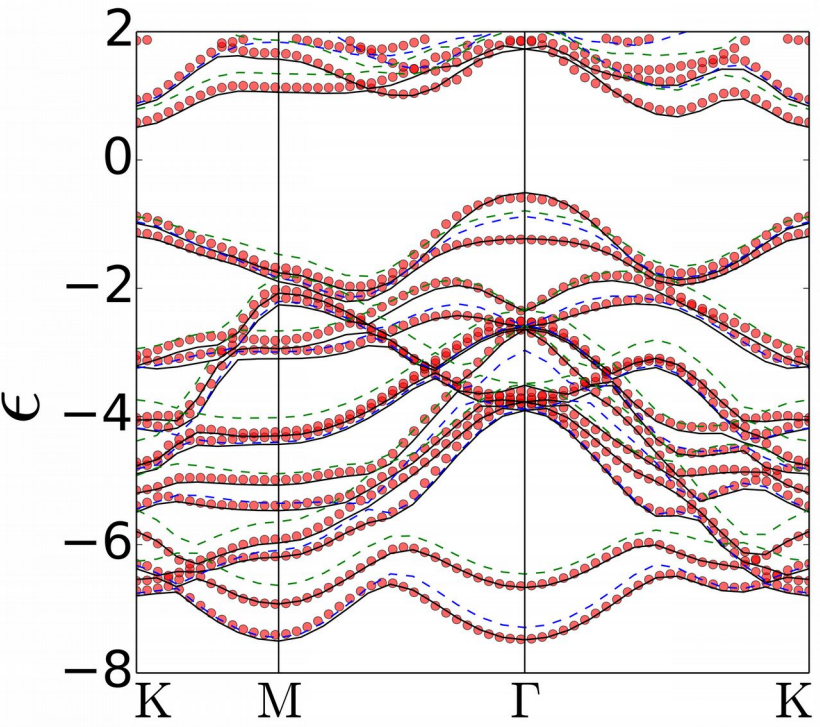
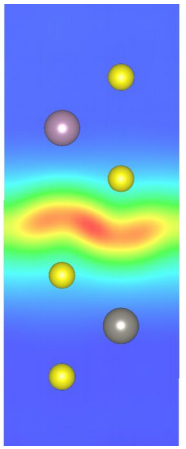
e) MoS_2/ WS_2

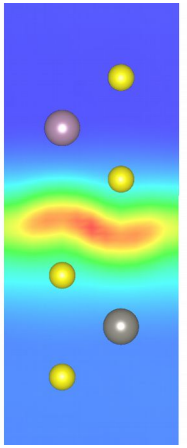


ΔV_{12}

DFT



Model

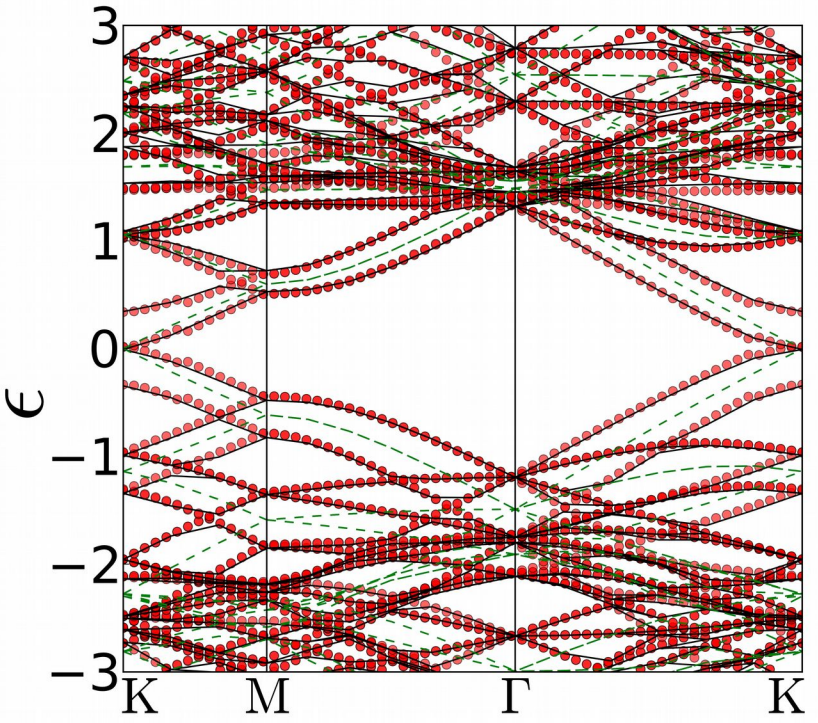


Model — DFT — Single layer DFT

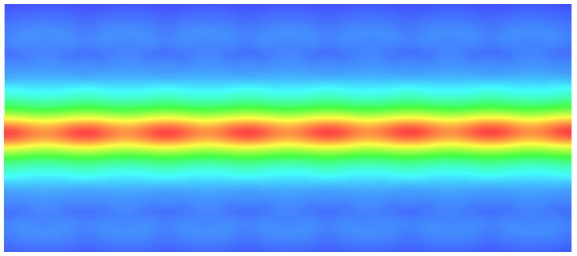
Energy	DFT	Model	Diff
Kinetic	1439.16	1440.69	1.53
Hartree	-34.23	-34.19	0.04
Exc	-40.80	-40.08	0.72

f) 7x7 Supercells

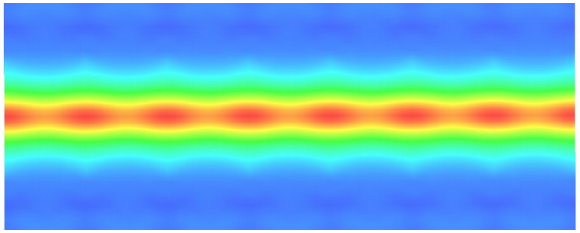
a) Gr/Gr (0^o rotation)



ΔV_{12}

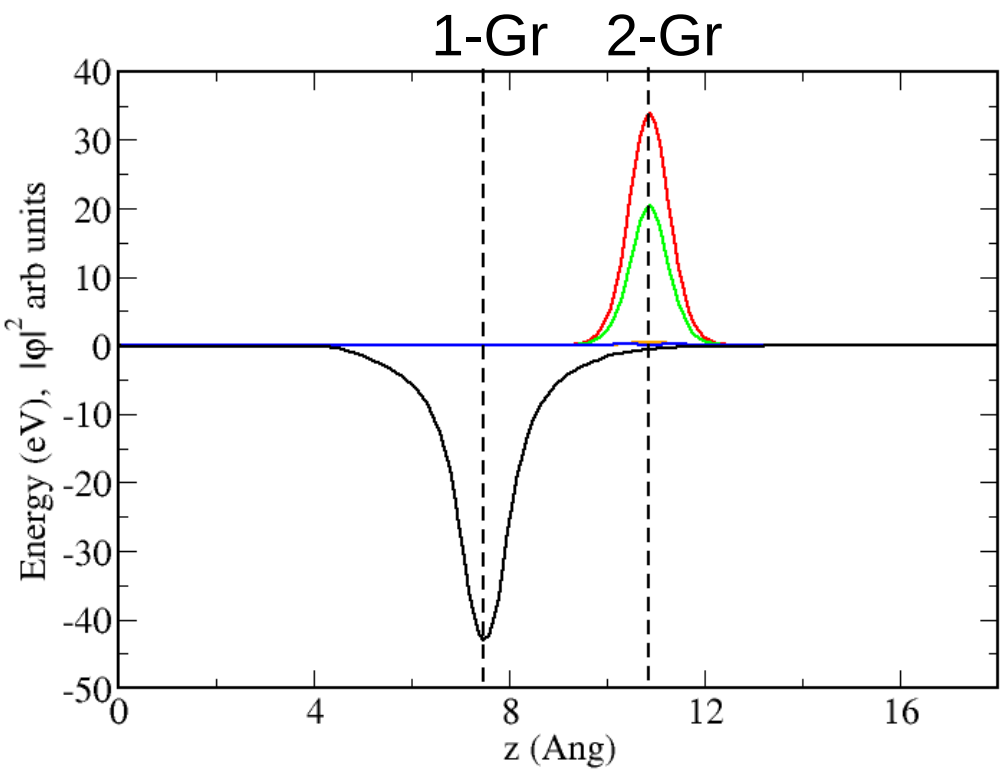


DFT

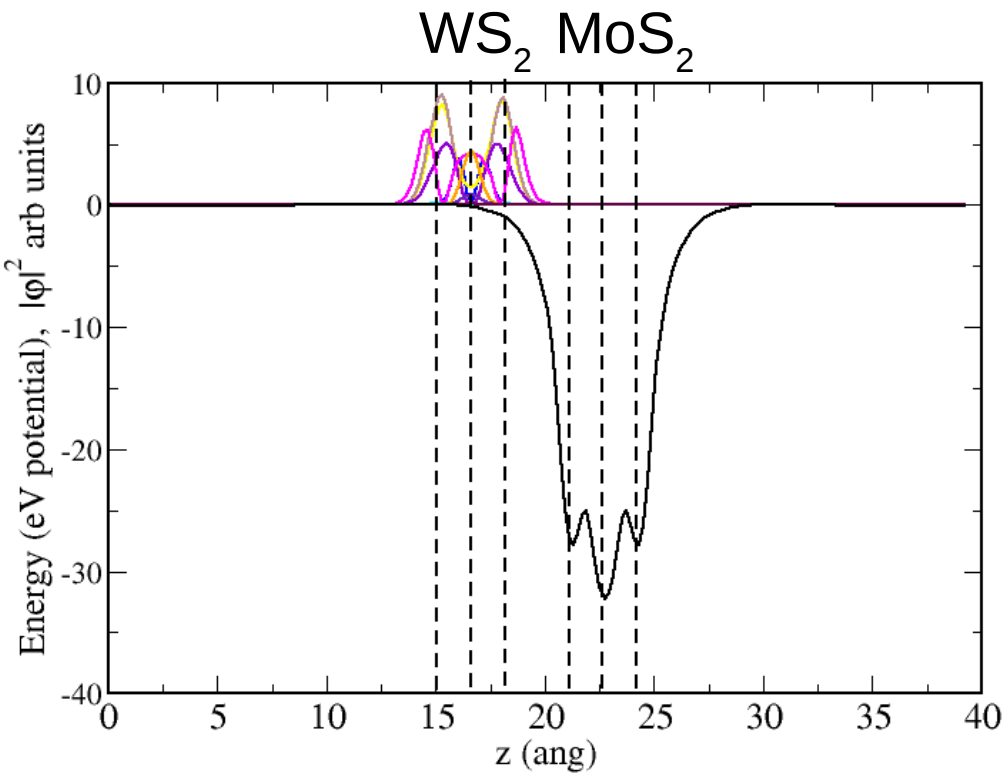


Model

Shortcomings



Occupied 'p' orbitals of layer 2
decay fast near potential of layer 1



Occupied 'd' orbitals of WS_2
do not decay fast near potential of MoS_2

- Occupied 'd' orbitals do not decay fast enough near the other layer
- Errors larger in MoS_2 as compared with Graphene

Conclusions

- Capability of the Code
  - Rotated and Unrotated structures
  - k-point grid and path in k-space
  - Generates DOS and Band structures
  - Extended to self-consistent calculations
  - Total Energy can be calculated
- No a priori knowledge of interaction potential required
- Errors ~ 50 meV w.r.t. DFT calculations
- Lattice mismatched / rotated incommensurate structures can be simulated without full DFT calculations!
- Future scope: heterostructures MoS_2, Black phosphorus, Gr ...

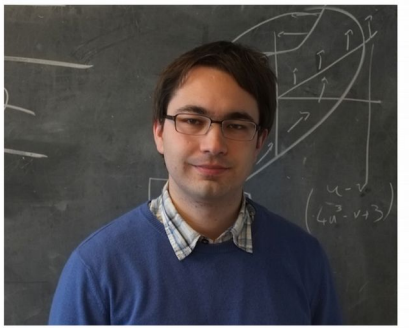
Acknowledgements

Efthimios Kaxiras

Georgios Tritsaris

Collaborators

Mitchell Luskin



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Petr Plechac

University of Delaware

Eric Cances

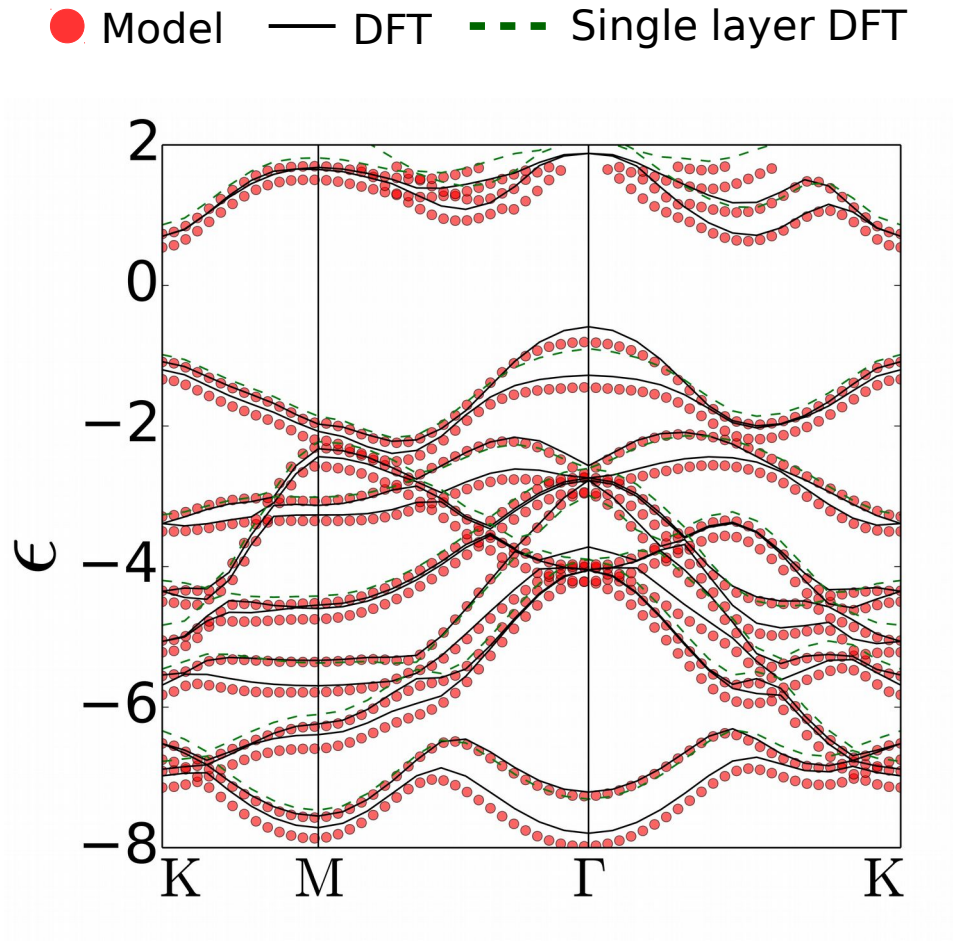
Ecole des Ponts

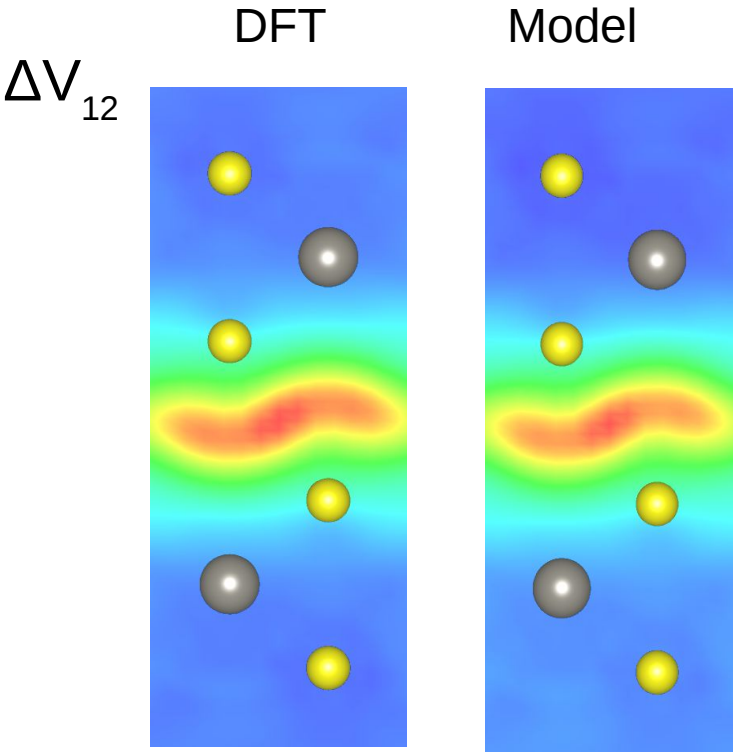
- ARO MURI Award W911NF-14-0247
- Odyssey cluster at Harvard University
- XSEDE

Thank you

Thank you

e) WS_2/ WS_2



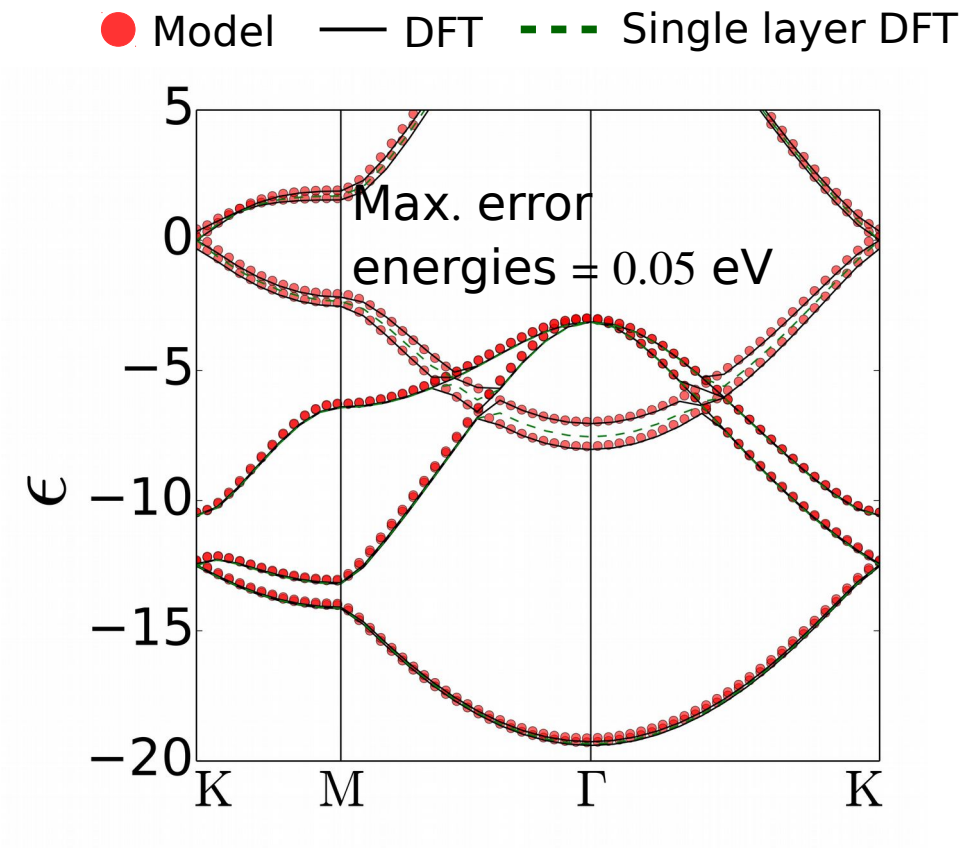


Energy	DFT	Model	Diff
Kinetic	1385.69	1386.77	1.08
Hartree	-46.22	-47.08	-0.86
Exc	-45.54	-45.65	-0.11

2) ΔV_{12}: Self-consistent

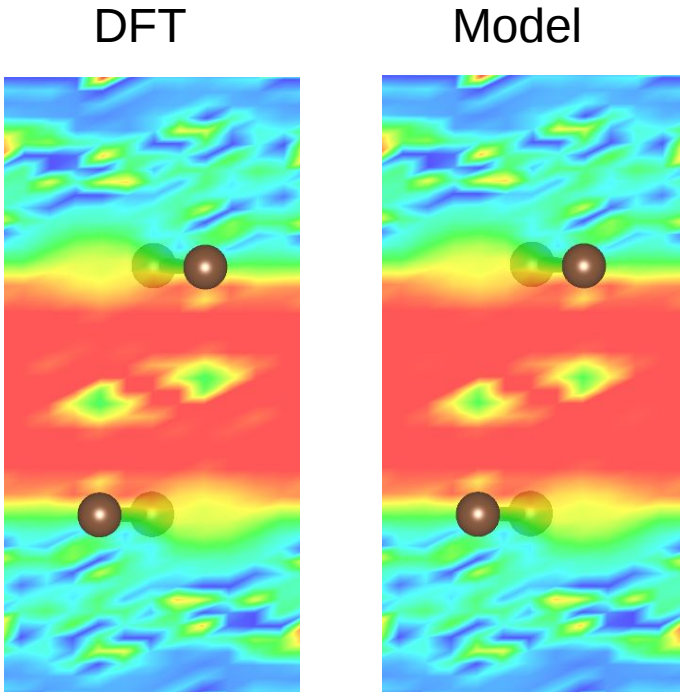
- Unit cells (AB stacked)

  a) Gr/Gr



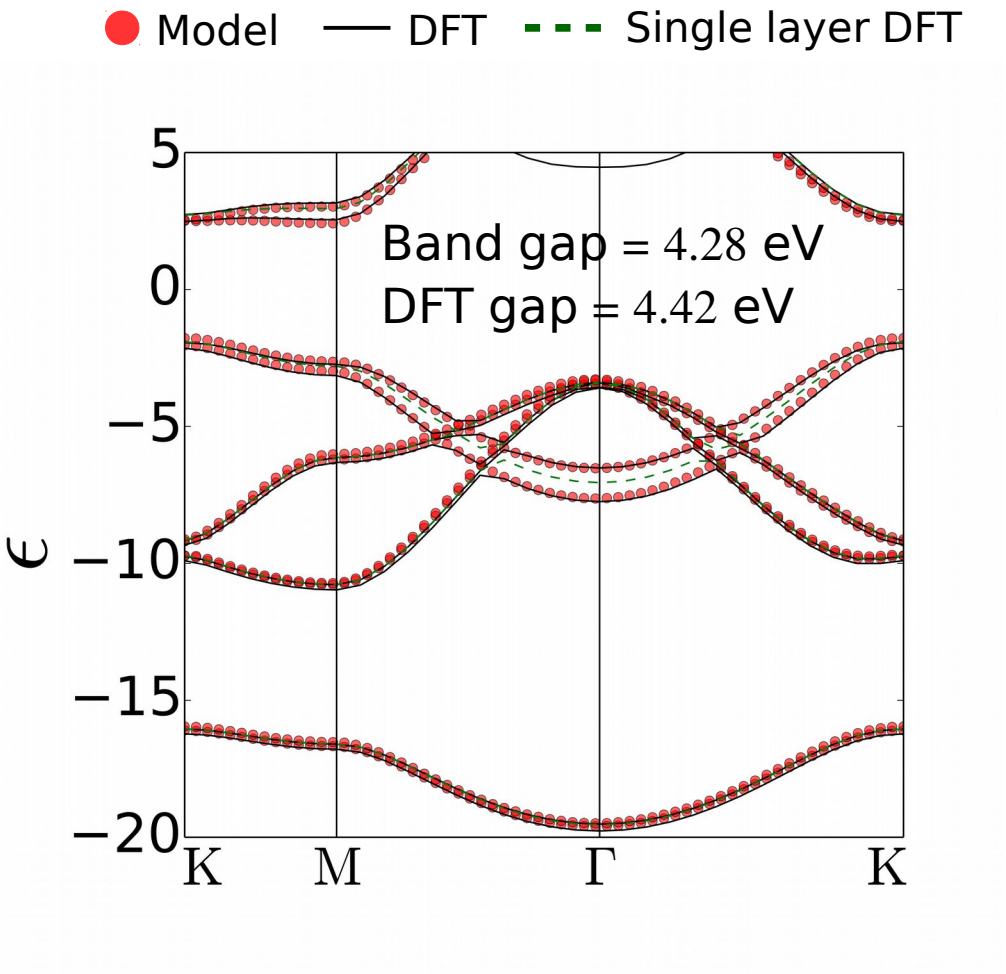
Calculation converged at first step!

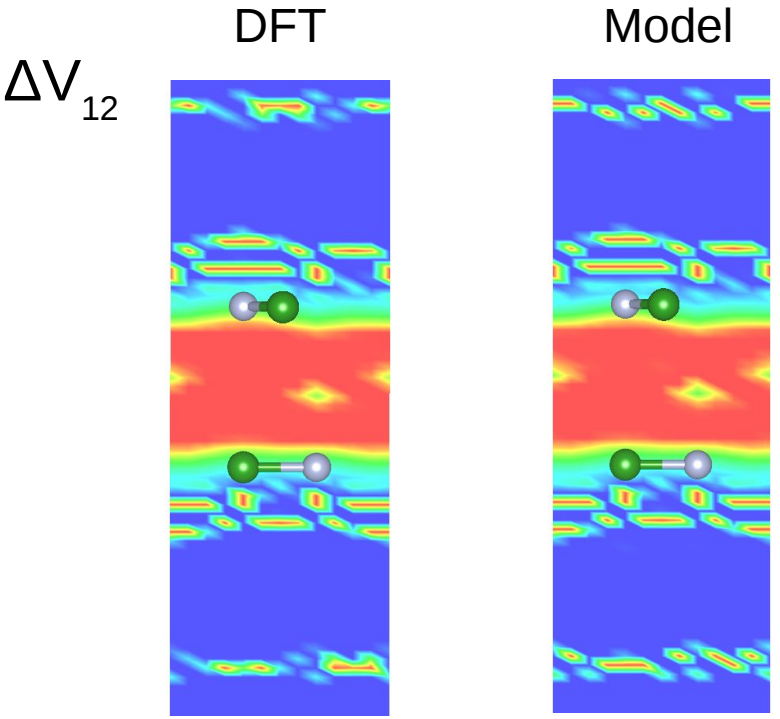
ΔV_{12}



Energy	DFT	Model	Diff
Kinetic	579.19	578.70	-0.49
Hartree	-33.25	-33.19	0.06
Exc	-52.10	-52.05	0.05

b) h-BN/h-BN



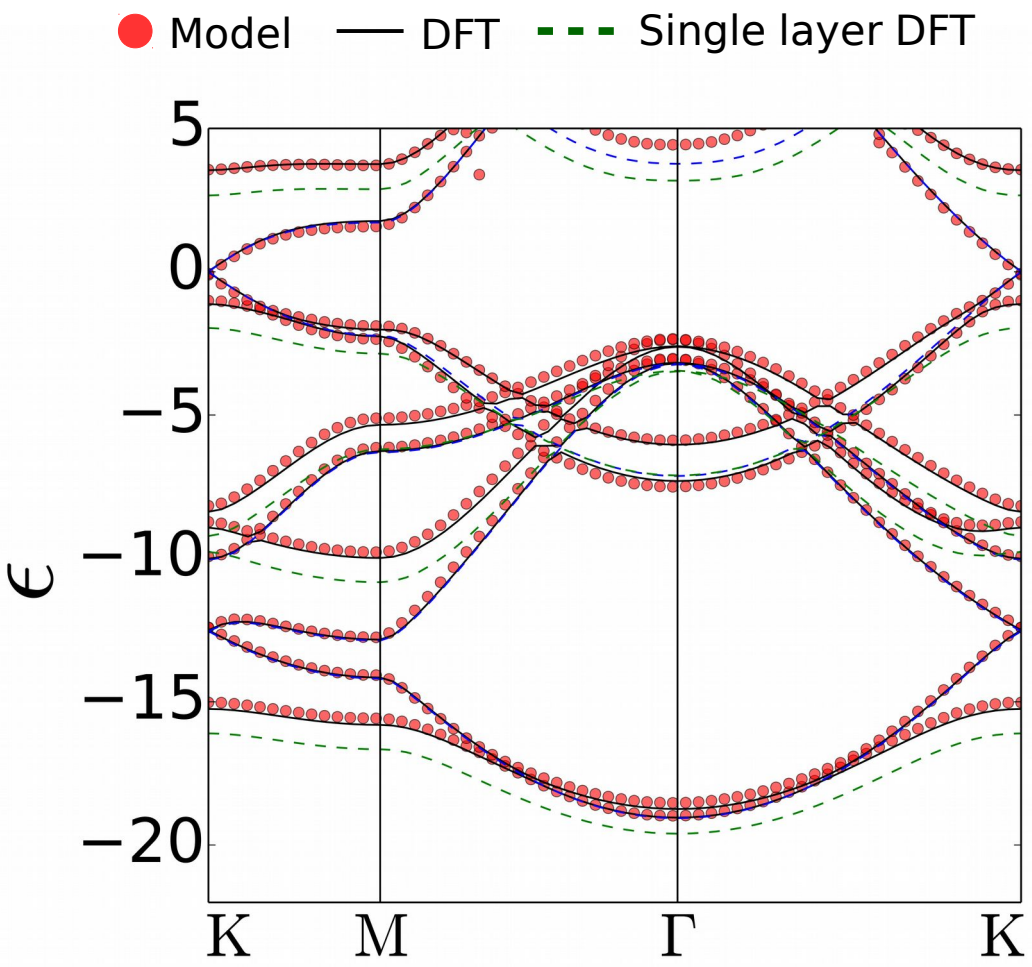


Energy	DFT	Model	Diff
Kinetic	648.82	647.70	-1.12
Hartree	-33.25	-34.53	-1.28
Exc	-51.84	-51.78	0.06

Error saturates at the first step.

Convergence is better for insulators!

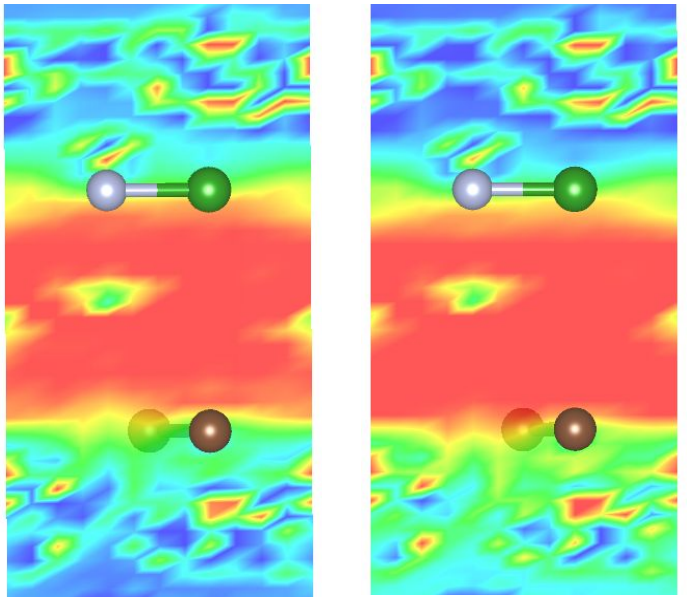
c) Gr/h-BN



Band gap = 0.047 eV

DFT gap = 0.034 eV

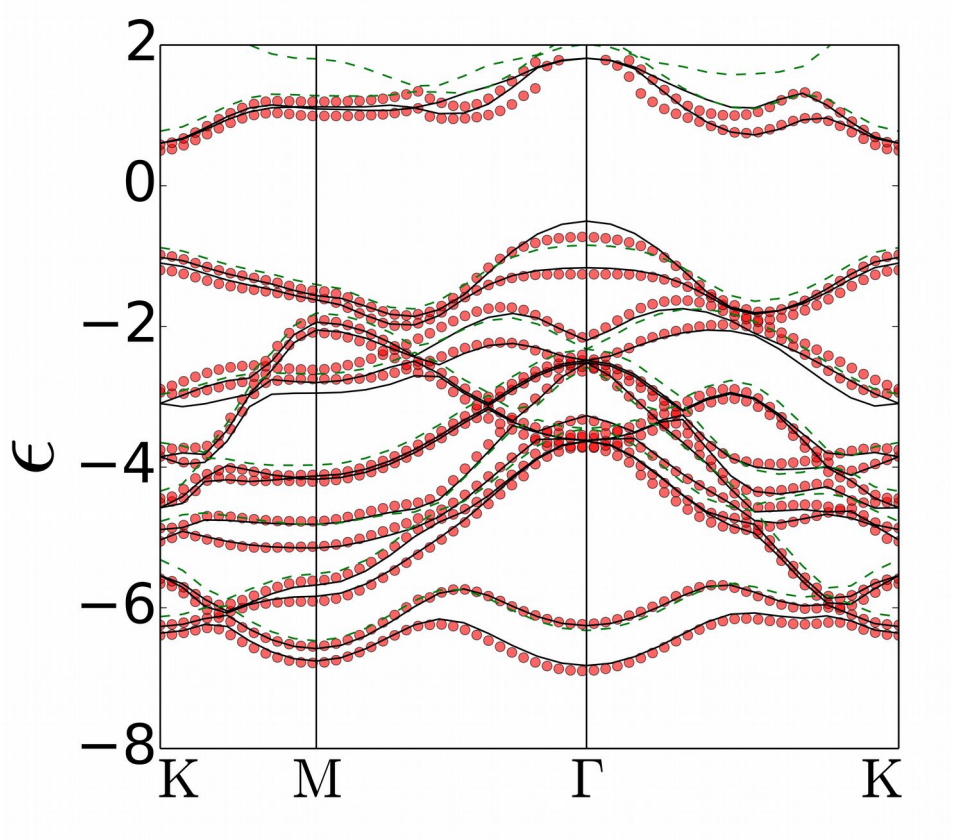
ΔV_{12}



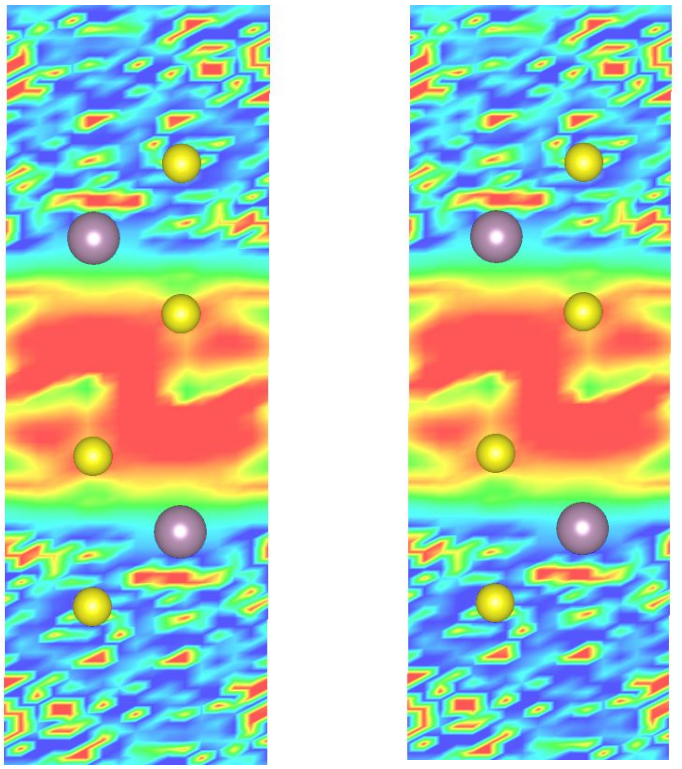
Energy	DFT	Model	Diff
Kinetic	648.82	647.70	-1.12
Hartree	-33.25	-34.53	-1.28
Exc	-51.84	-51.78	0.06

d) MoS_2/ MoS_2

Model — DFT - - - Single layer DFT



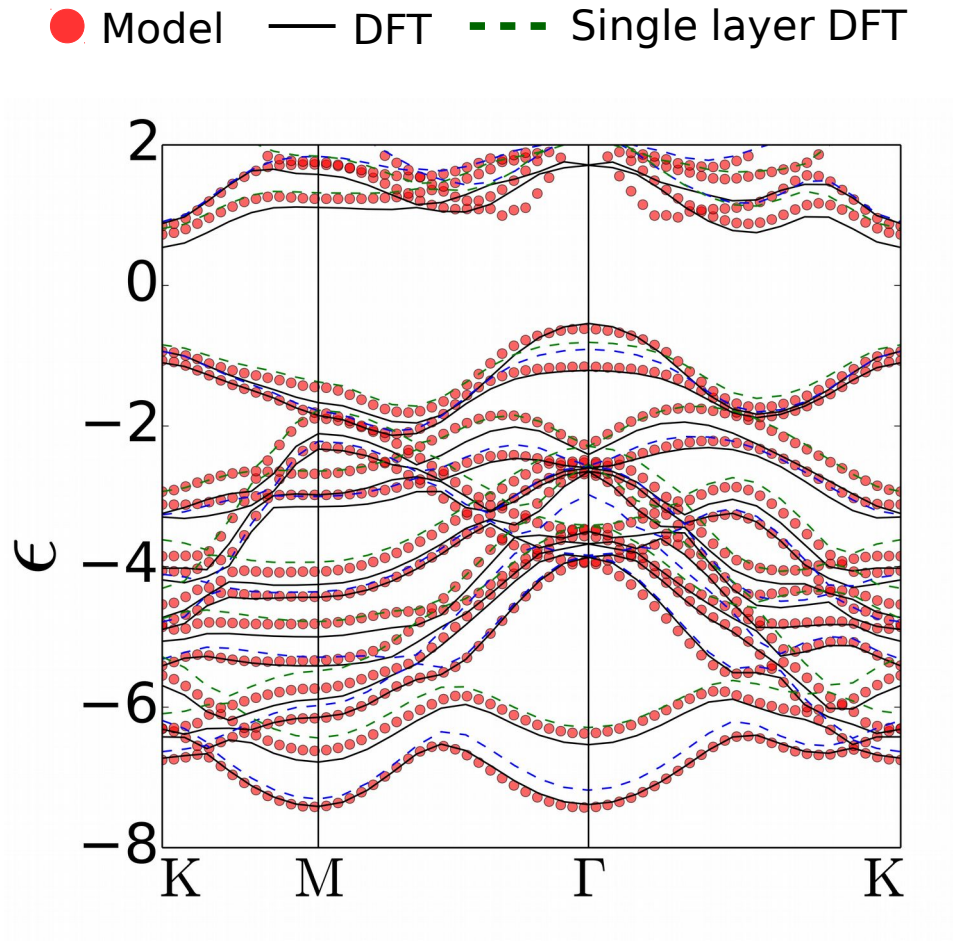
ΔV_{12} DFT Model

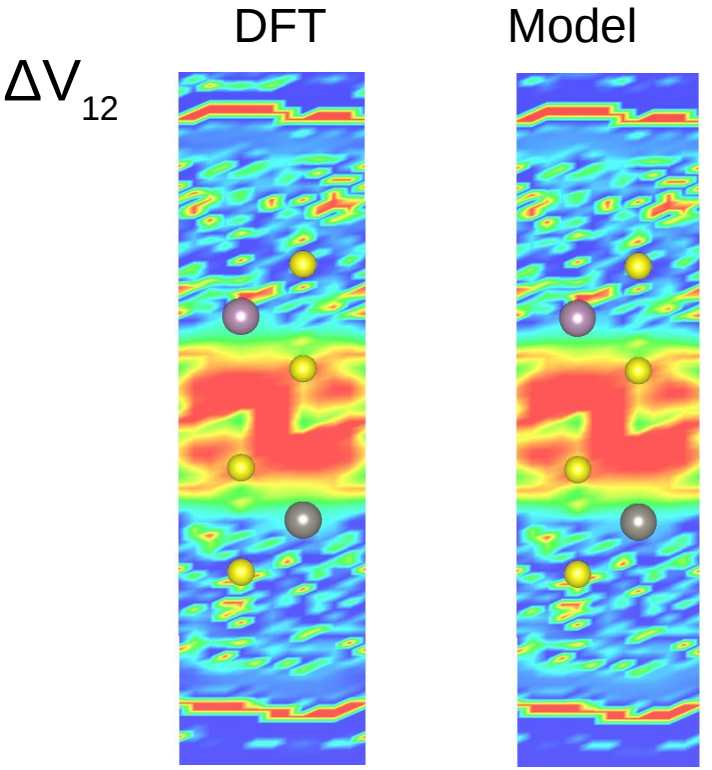


Energy	DFT	Model	Diff
Kinetic	1502.2	1502.7	0.5
Hartree	-61.06	-60.42	-0.36
Exc	-187.34	-187.23	0.11

Error larger than Gr-Gr.
The band structure is well represented!

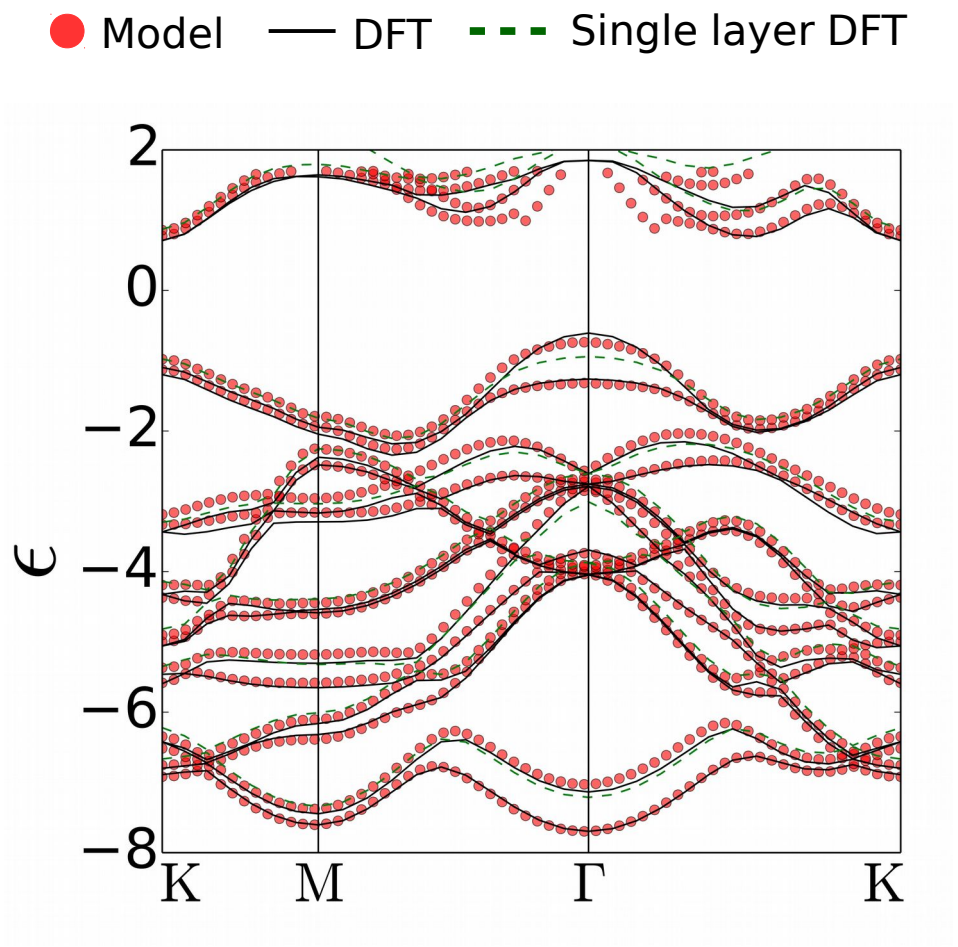
e) MoS_2/ WS_2

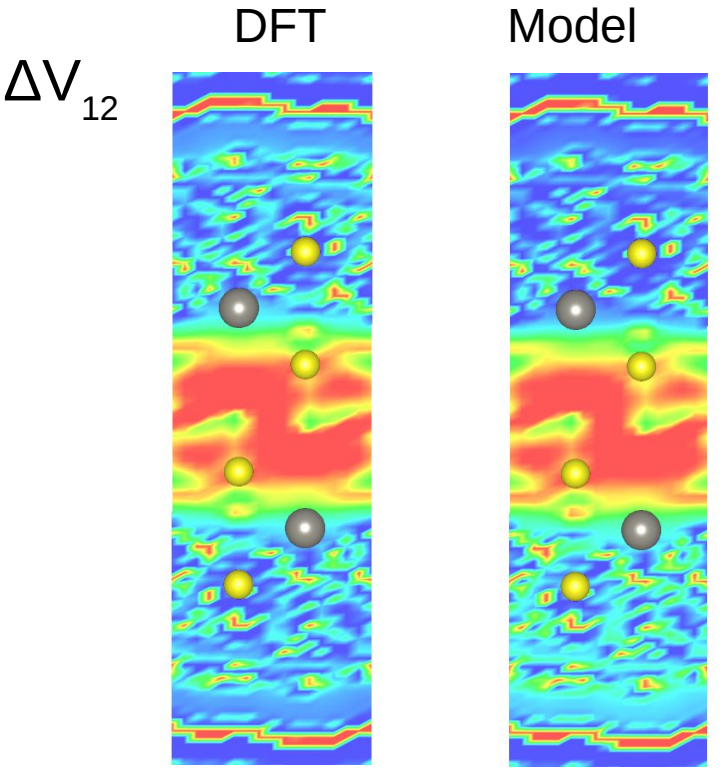




Energy	DFT	Model	Diff
Kinetic	1446.56	1447.09	0.53
Hartree	-74.31	-72.80	1.51
Exc	-231.49	-231.26	0.23

f) WS_2/ WS_2

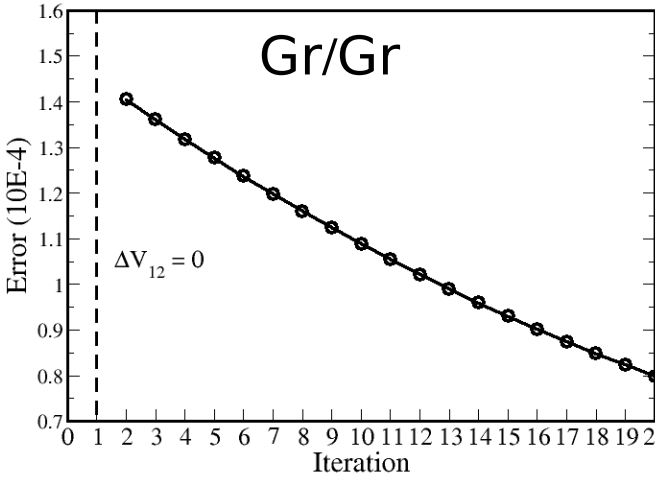


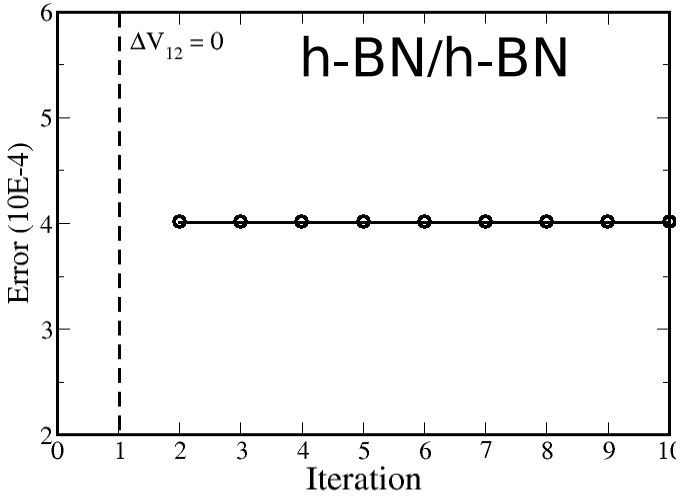


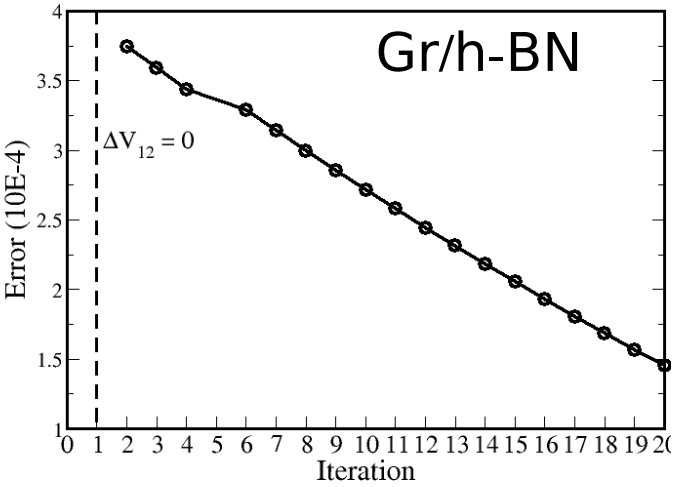
Energy	DFT	Model	Diff
Kinetic	1391.90	1387.75	-4.5
Hartree	-86.46	-85.70	0.76
Exc	-275.60	-275.48	0.12

Error = $| \int (\rho_{in} - \rho_{out})\, dr |$

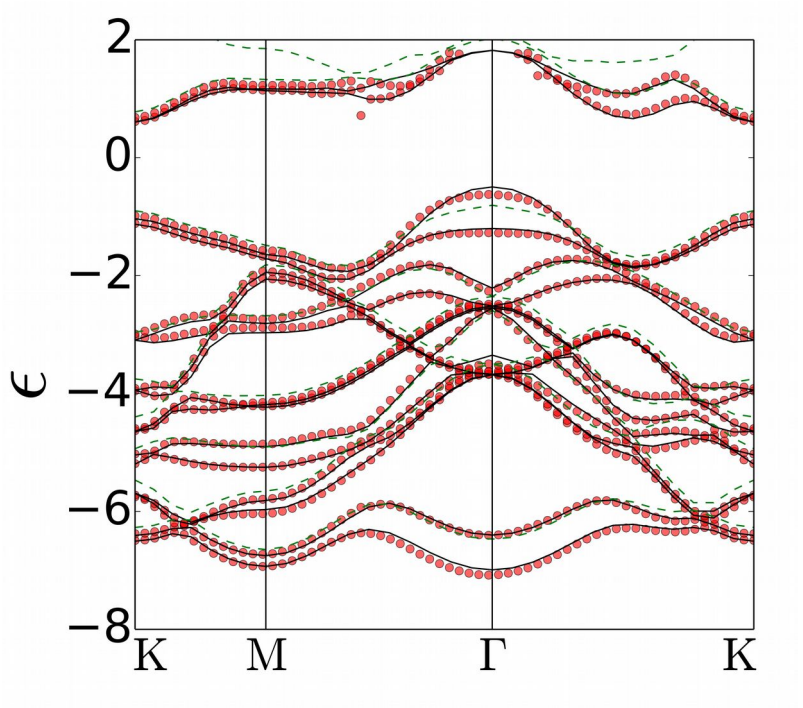
Error decreases linearly



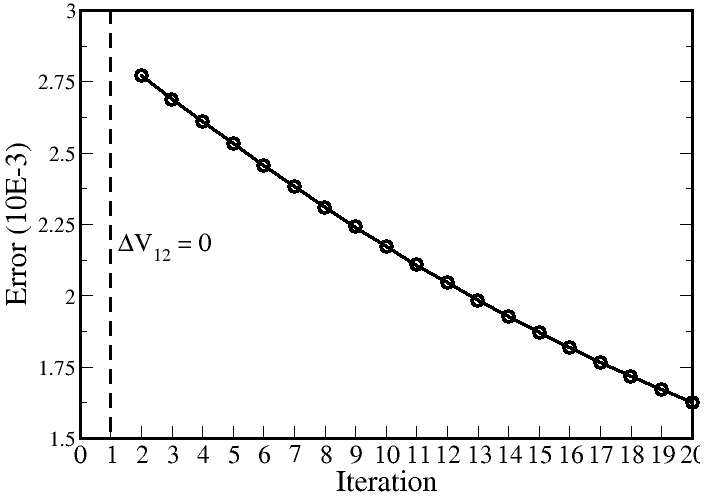




Self-consistent results agree well with DFT!



MoS_2/ MoS_2



ΔV_{12}

DFT Model