Solving Kohn-Sham Equations of Heterobilayer Systems Beyond 1000 Atoms: Twist Angle-dependent Piezoelectricity

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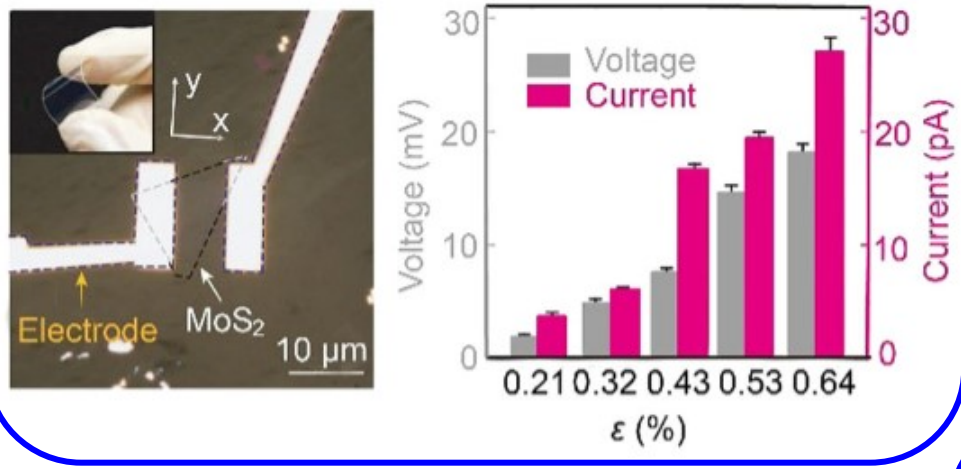
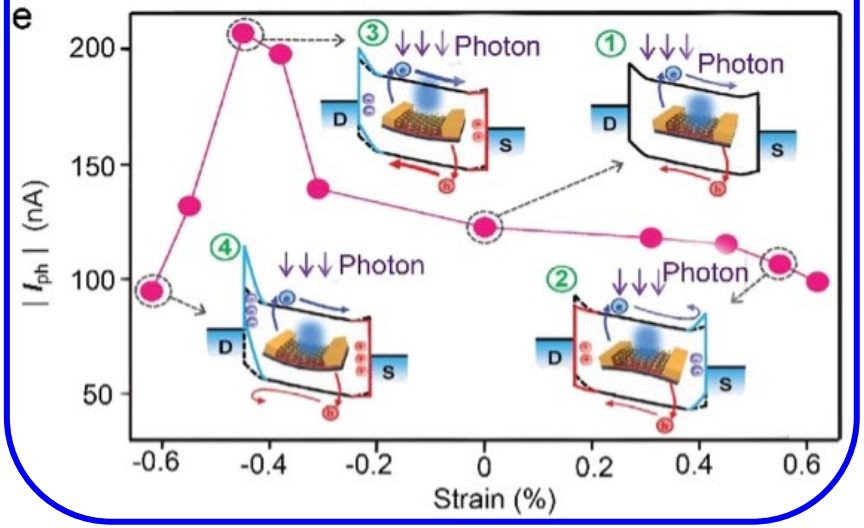
Motivation - Applications

Applications of 2D piezoelectric materials:

Energy harvesting (nanogenerator)



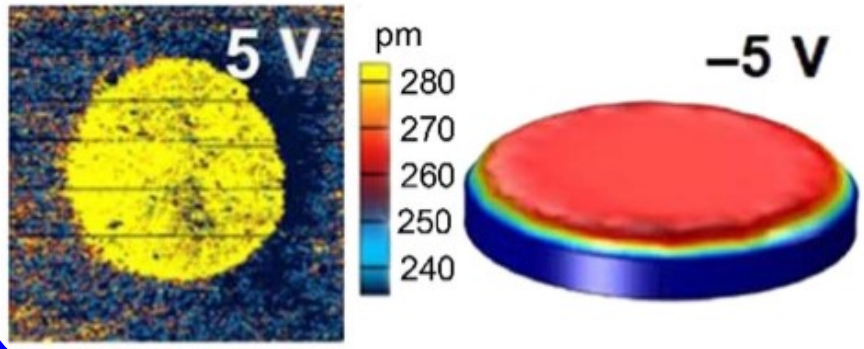
Piezophototronic



Stacking 2D materials allows more functionalization possibilities

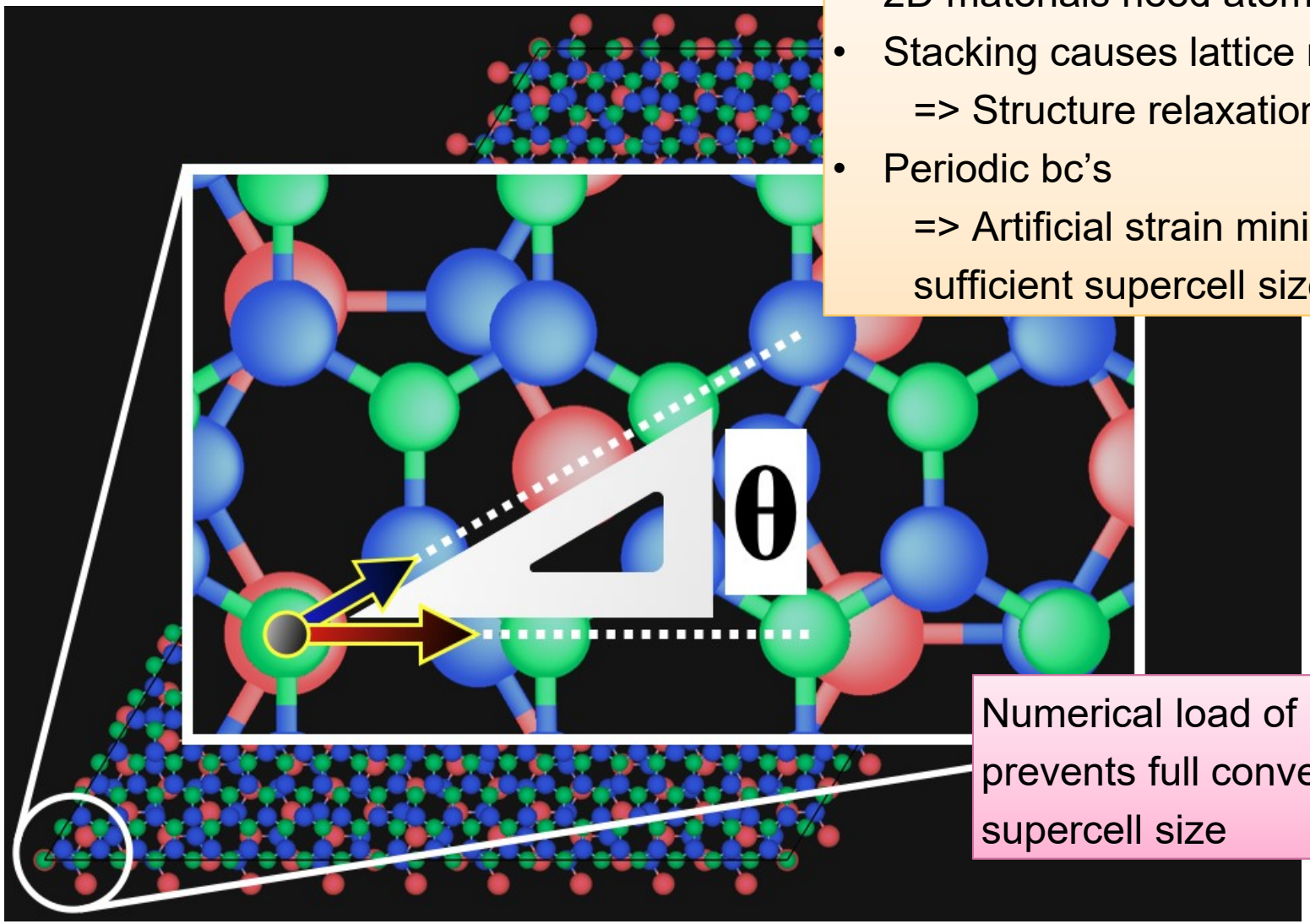
Twist angle offers a new degree of freedom!

Actuator



Chaojie Cui et al, Two-dimensional materials with piezoelectric and ferroelectric functionalities, Nature, 2018

Motivation - Modeling Challenge



- 2D materials need atomic resolution
- Stacking causes lattice mismatch
  => Structure relaxation
- Periodic bc's
  => Artificial strain minimized with sufficient supercell size

Numerical load of DFT typically prevents full convergence w.r.t supercell size

Method

The total energy given in DFT (Kohn-Sham method):

$$E = T_o[\rho] + \int V_{ext}\rho(\vec{r})d\vec{r} + \frac{1}{2}\int \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r}' - \vec{r}|}d\vec{r}d\vec{r}' + E_{xc}[\rho]$$

$E_{kinetic}$ non interacting

E_{ne}

$E_{coulomb}$ E_{ee}

E_{xc} exchange-correlation

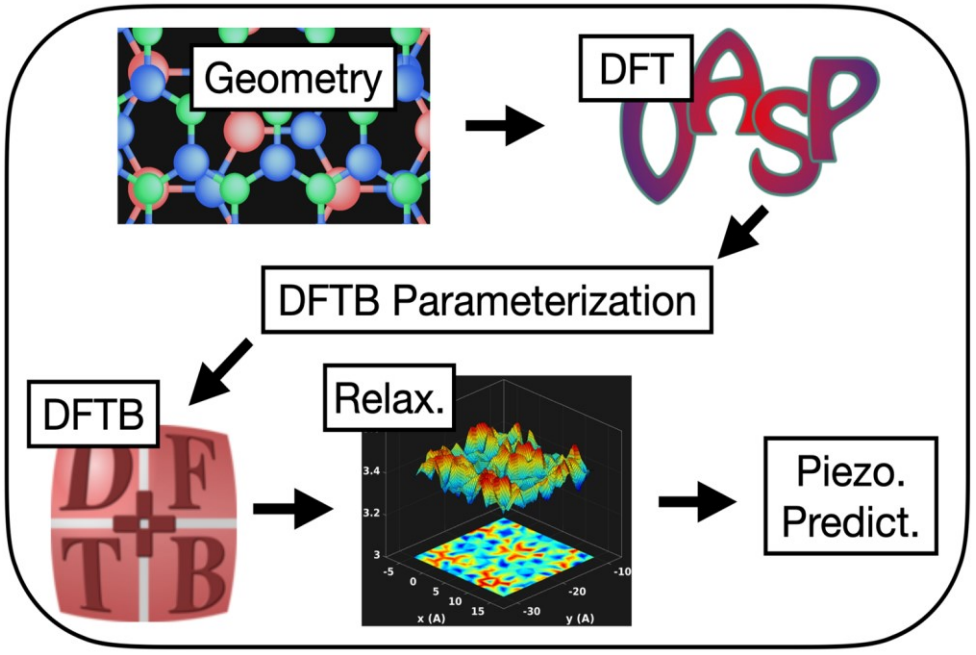
Repulsive Potentials

DFTB Energy
(Electronic Parameters: On-site energies, compression radii, etc.)

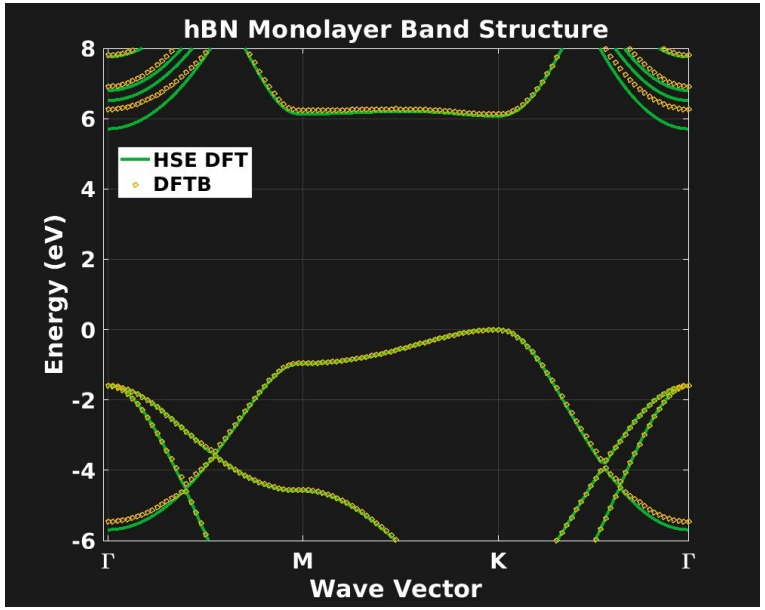
This method:

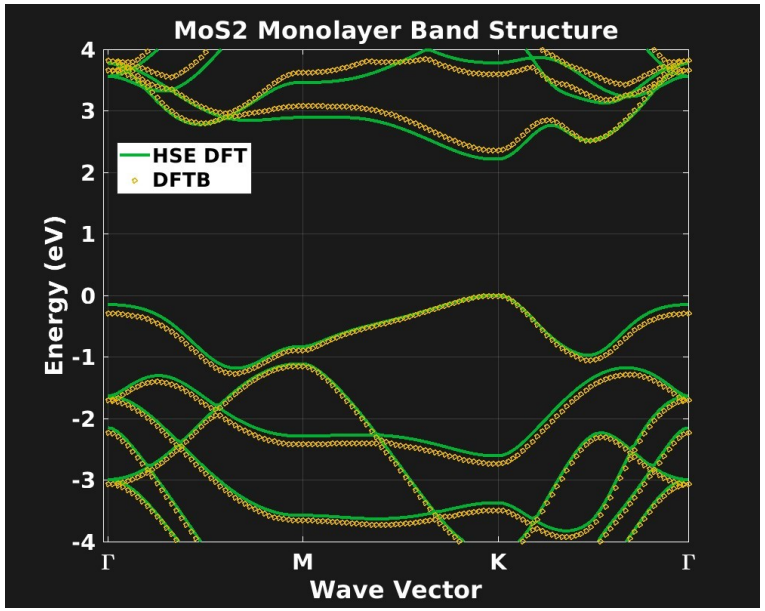
- Structure relaxation while solving Kohn-Sham equations of sufficiently large structures
- DFTB parameters fit to reproduce DFT HSE06 results

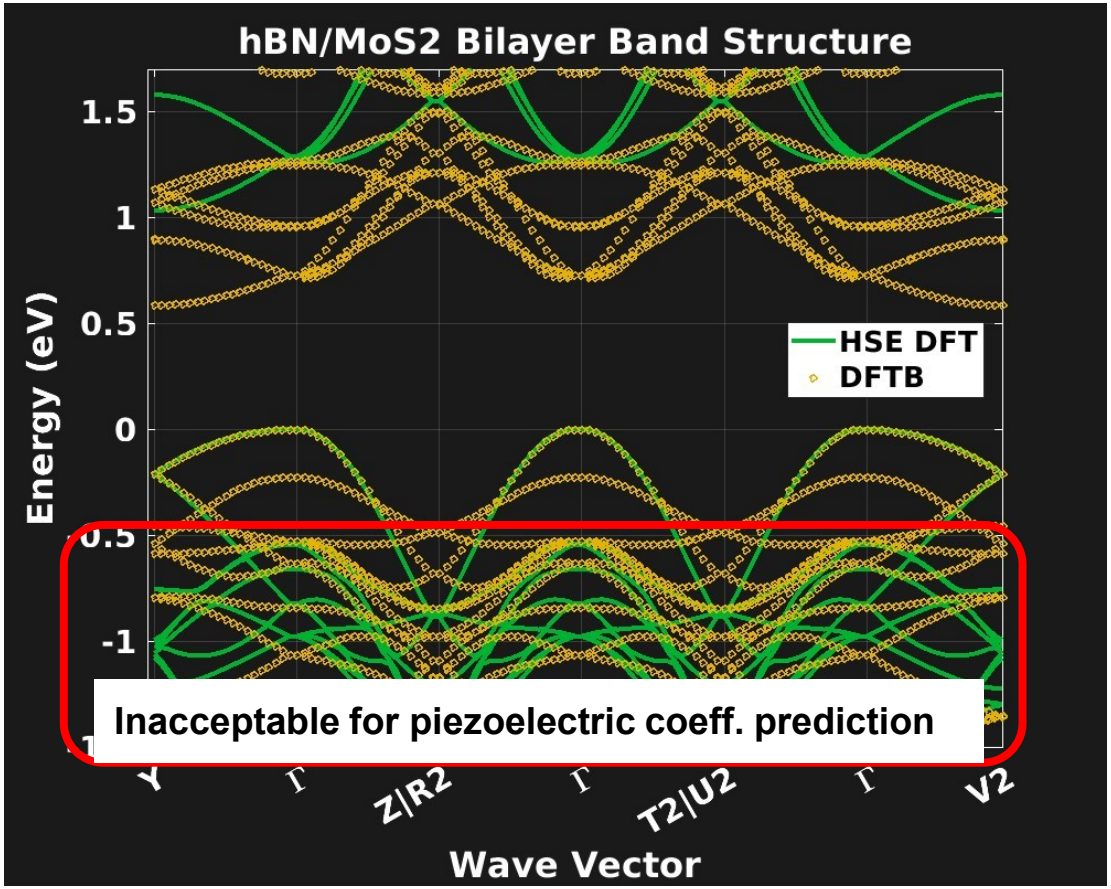
Method flow diagram



Results: Parameter Transferability

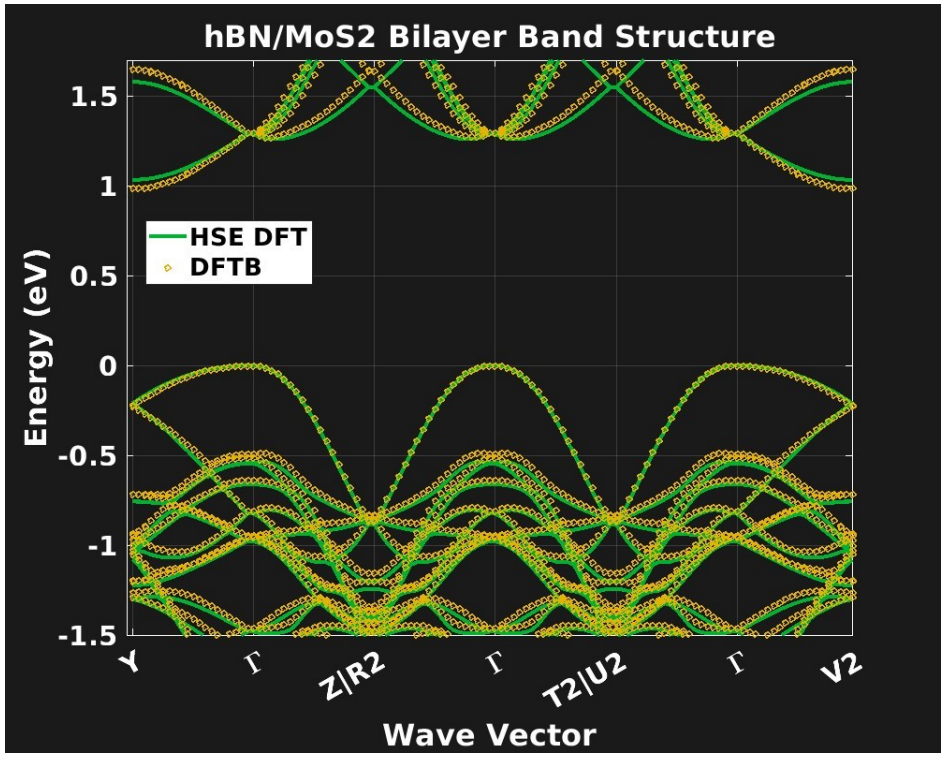


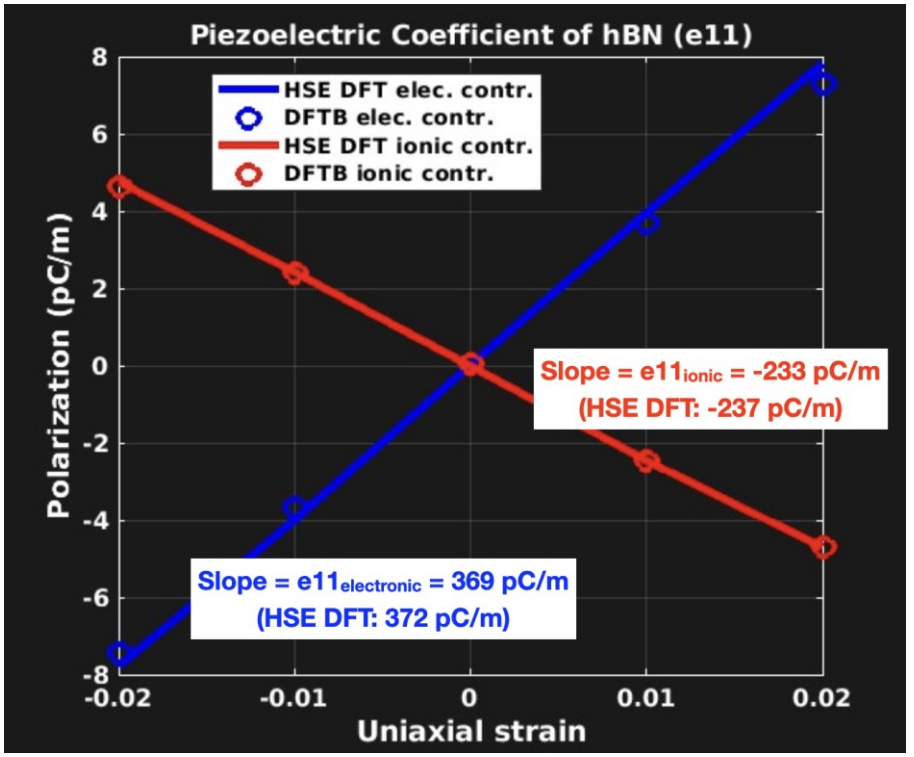




- Parameters are not transferable between monolayer and bilayer structures
- All parameters are fitted simultaneously for each system respectively

Results: Parameterization





DFTB vs. HSE06 DFT:

✓ DFTB parameters are transferable between monolayer and bilayer structures

✓ Deep lying valence bands reproduced

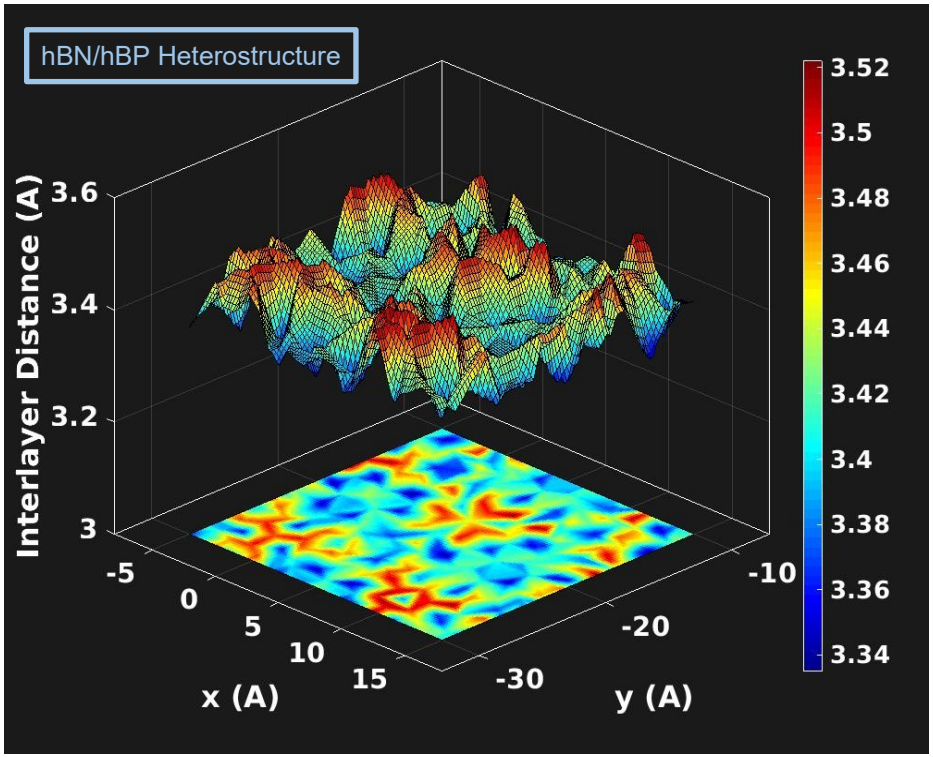
✓ Piezoelectric coefficients agree with DFT calculations in small systems

HSE DFT: elec. contr. e11 = 372 pC/m, ionic contr. -237 pC/m

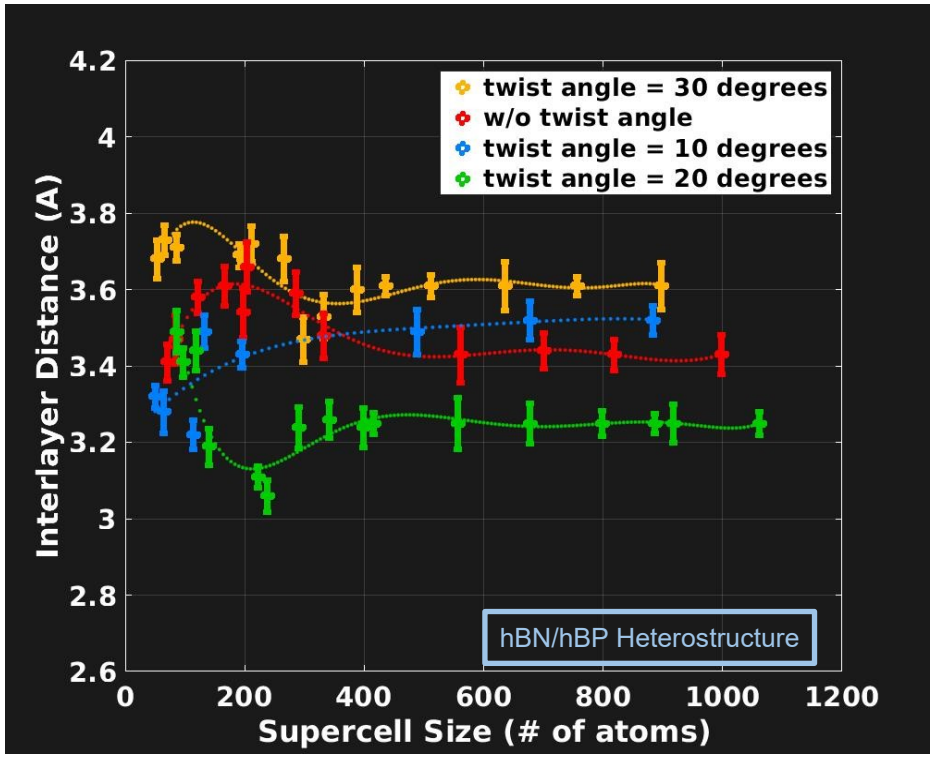
DFTB: elec. contr. e11 = 369 pC/m, ionic contr. -233 pC/m

Result: Convergence vs. Supercell Size

Corrugation Field @ θ = 10 degrees



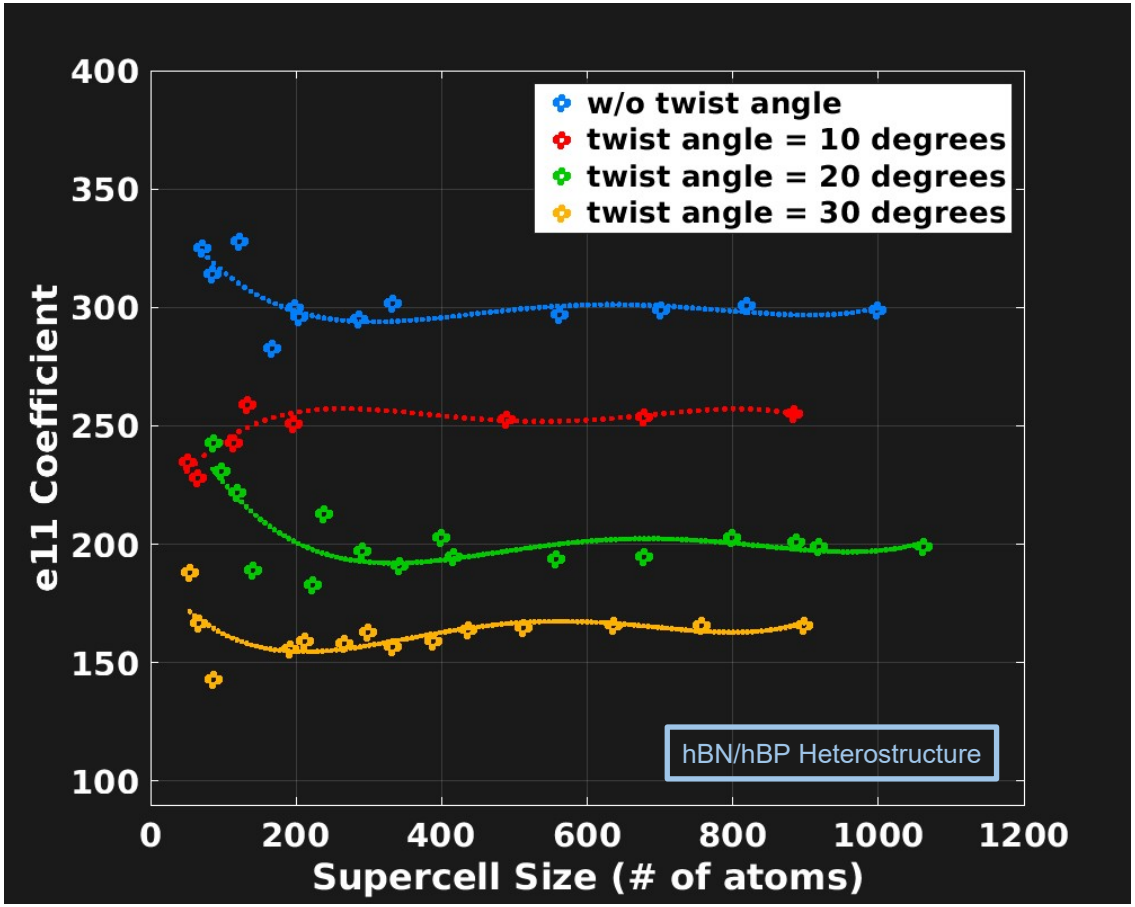
Averaged Interlayer Distance vs. Cell Size



- ✓ Artificial boundary effects are avoided with sufficient supercell sizes
- ✓ Supercells containing ~1000 atoms are possible with DFTB
- ✓ Typical minimum ~600 atoms (angle dependent)

Result: Convergence vs. Supercell Size

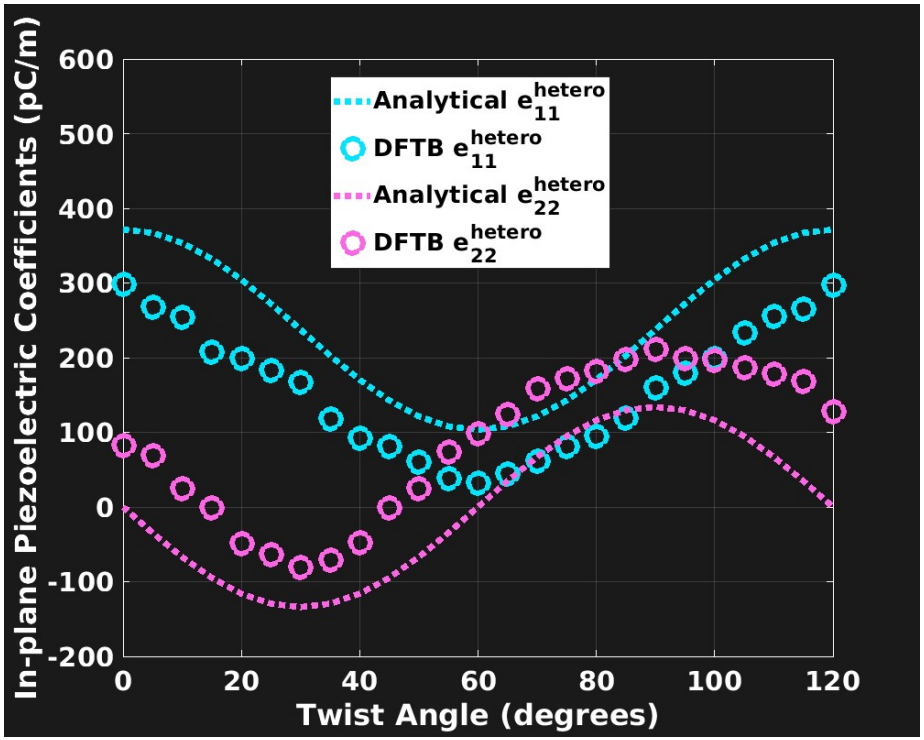
In-plane Piezoelectric Coefficient



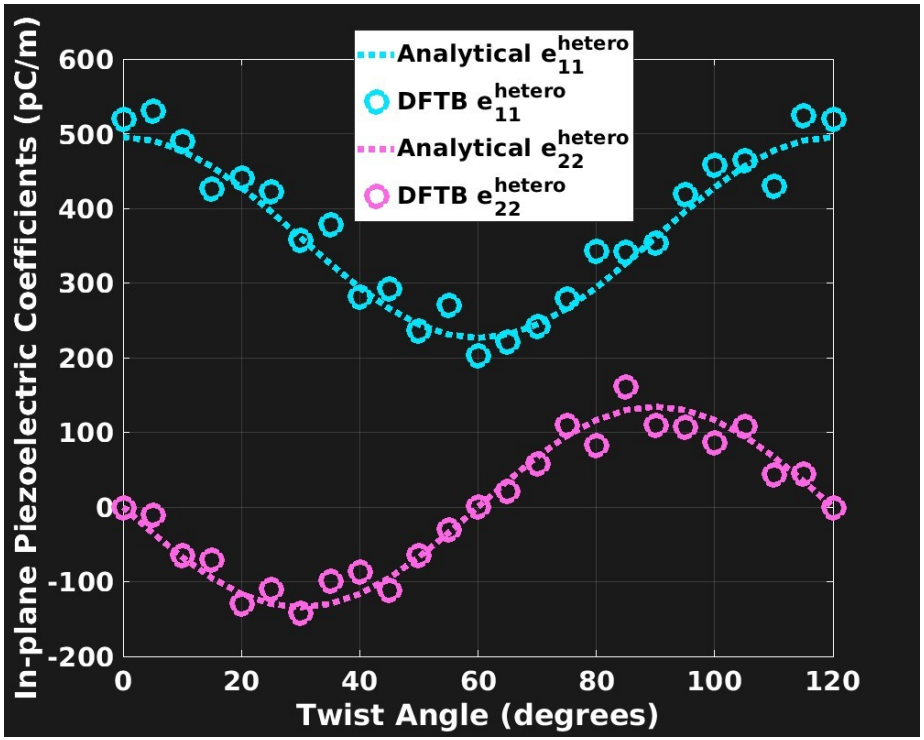
✓ Piezoelectric coefficient converges with supercell size

Result: In-plane Piezoelectric Coefficients

hBN/hBP Heterostructure



hBN/MoS2 Heterostructure



Analytical Model (perfect sym.)

$$e_{11}^{\text{Hetero}} = e_{11}^{\text{hBN}}\cos(3\theta) + e_{11}^{\text{MoS2/hBP}}$$

$$e_{22}^{\text{Hetero}} = -e_{11}^{\text{hBN}}\sin(3\theta) + e_{22}^{\text{MoS2/hBP}}$$

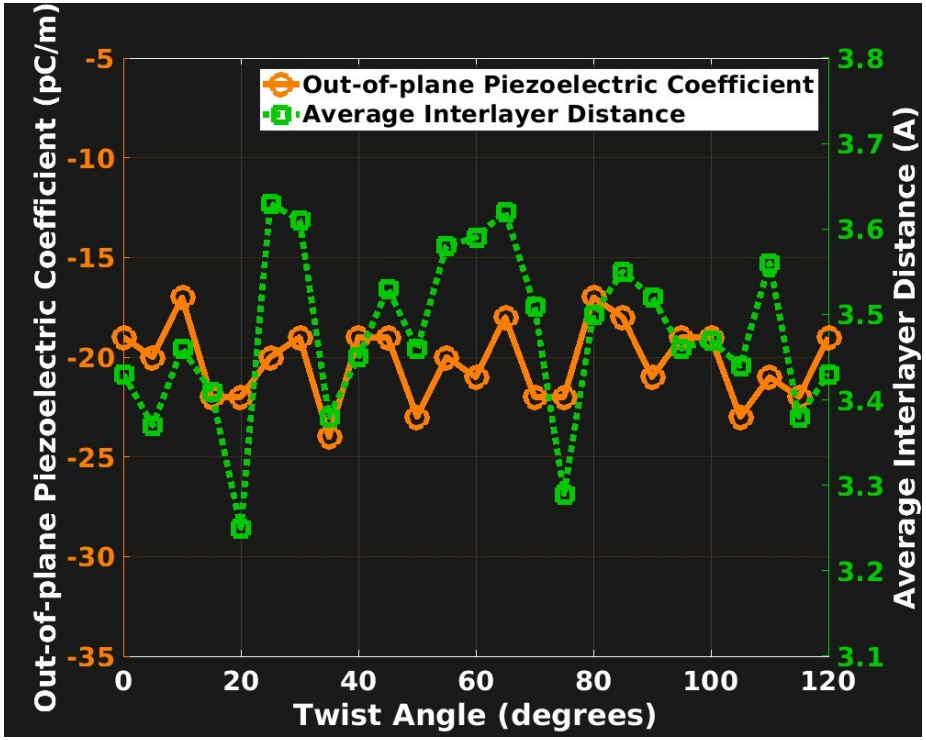
- Material symmetry (here: 120-degree) reproduced
- Deviation from symmetry due to interlayer charge transfer, corrugation, twist-angle dependence, etc.

Relevant for device design: In-plane piezoelectric coefficients are tunable

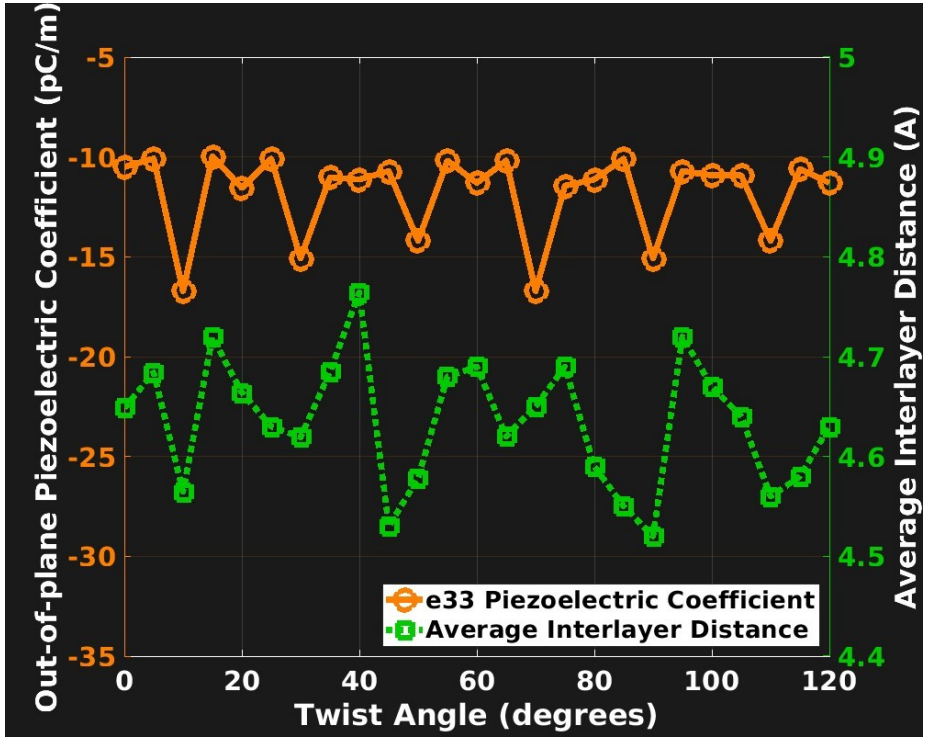
Result: Out-of-plane Piezoelectricity

Out of plane response due to broken inversion symmetry along z expected

hBN/hBP Heterostructure



hBN/MoS2 Heterostructure



Finite out-of-plane piezoelectricity confirmed

Conclusion

This talk:

✓ Introduction of method for reliable and efficient piezoelectricity prediction of 2D heterobilayer systems

✓ The method guarantees convergence of results vs. system size

Take home message:

- Large enough supercell is required for piezoelectricity prediction
- In-plane piezoelectric coefficients are tunable
- Finite out-of-plane piezoelectric response confirmed

Thank you!