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

Han-Wei Hsiao, Namita Narendra, and Tillmann Kubis
Elmore Family School of Electrical and Computer Engineering, Purdue University, West Lafayette, IN, USA
e-mail: hsiao35@purdue.edu

Abstract

We introduce an efficient density-functional tight-binding (DFTB) approach that allows converged piezoelectric coefficient predictions of relaxed, twisted two-dimensional (2D) heterobilayer systems beyond 1000 atoms on a single compute node. The results unveil controllable in-plane piezoelectricity in twisted hBN/hBP heterobilayers. The corresponding out-of-plane piezoelectric response, on the other hand, is mostly constant due to corrugations. We apply and extend this method to study twist angle-dependent piezoelectricity in hexagonal III-V/transition metal dichalcogenide (TMD) van der Waals heterostuctures.

Introduction

Recent studies have demonstrated that stacking 2D monolayers may achieve a stronger piezoelectricity than the sum of the respective monolayers [1], [2]. There is experimental evidence that suggests that the twist angle is a relevant design and control factor for the piezoelectric coefficients of van der Waals heterostructures [3], [4]. This theoretical work assesses in high detail the impact of the twist angle on the piezoelectricity of 2D heterobilayer systems. We expand the DFTB method to predict the piezoelectric coefficients of twisted and corrugated 2D heterostructures with more than 1000 atoms. We showcase the method on twisted hBN/hBP heterostructures (see Fig. 1). Our calculations yield a periodic relationship between the in-plane piezoelectric coefficients and the corresponding twist angles. In contrast, the twist angle influences the average interlayer distance which in turn determines the out-of-plane piezoelectricity.

Method

We apply the third-order self-consistent DFTB method implemented in the DFTB+ software to solve the Kohn-Sham equations of systems beyond 1000 atoms [5]. The DFTB parameters (compression radii, exponents, on-site energies) and the internuclear repulsion energies are parameterized to precisely reproduce the electronic structures and the piezoelectric coefficients predicted by the hybrid HSE06 functional implemented in VASP [6]. All relevant long-range effects due to twist angles, corrugations, and strain effects are well-converged vs. the supercell size.

Results and Discussion

Fig. 2 indicates that the interlayer distance gradually converges with the supercell size. This convergence affects all observables including piezoelectric coefficients. Initial supercells containing $1000+$ atoms are required for a well-converged simulation. Fig. 3 shows that the calculated in-plane piezoelectric coefficients of the twisted bilayers deviate from the idealized analytical results for all twist angles due to charge transfer, break of inversion symmetry, corrugations, and nonlinear, twist angle dependence. The out-of plane piezoelectric response correlates with the average interlayer distance. That in turn fluctuates with the layer corrugations and depends nonlinearly on twist angles which prevents a smooth angle dependence (see Fig. 4).

Conclusion

The prediction of twist angle dependent piezoelectric coefficients of heterobilayers converges with supercell sizes of around 1000 atoms only. Our

calculations show that the in-plane piezoelectricity varies strongly with the twist angle. The out-of-plane piezoelectric response does not show systematic twist angle dependence due to pronounced corrugation. This method is currently being used to explore non-linear twist angle-dependent piezoelectricity in other 2D material combinations (e.g., hexagonal III-V/TMD heterobilayers).

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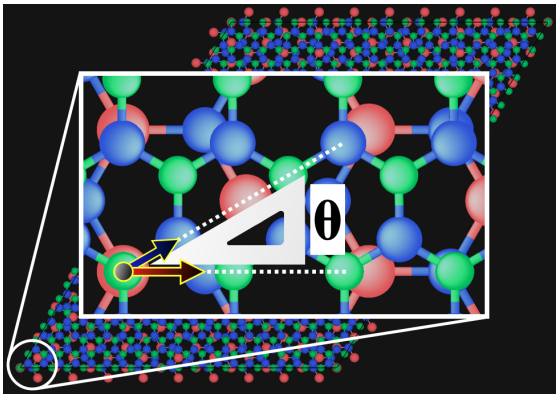

Fig. 1. Schematic of hBN/hBP heterostructure. The angle θ between the dipole vectors of hBN and hBP is the twist angle.

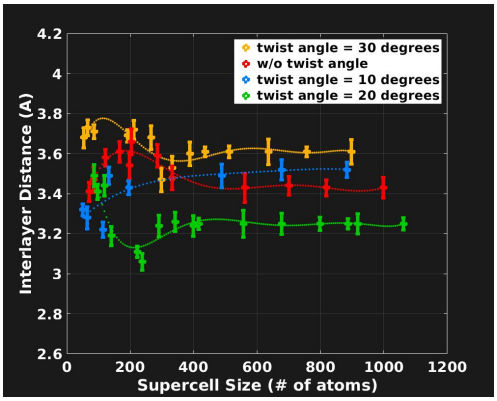

Fig. 2. Average interlayer distance as a function of supercell size. Typically, a supercell containing $\sim$ 1000 atoms is necessary for well-converged simulations.

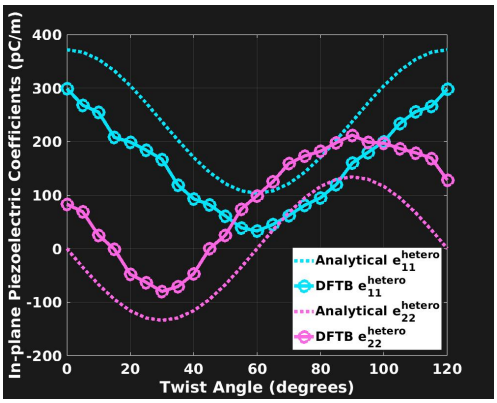

Fig. 3. In-plane piezoelectric coefficients e_{11} (blue) and e_{22} (red) vs. twist angle. The solid lines and the dotted lines are the DFTB results and the analytical formulas derived from isolated monolayers respectively.

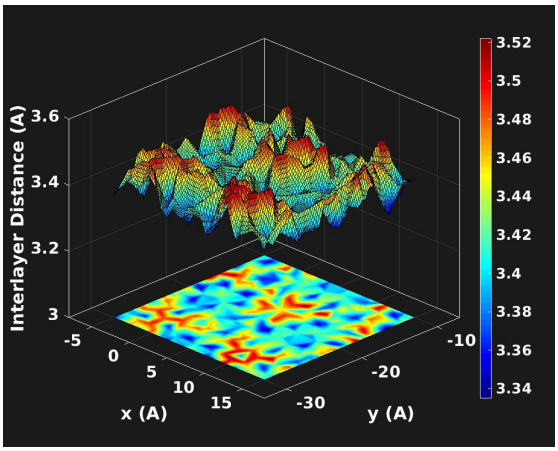

Fig. 4. Average interlayer spacing of the corrugated hBN/hBP heterobilayer twisted at $\theta = 10$ degrees. The interlayer spacing varies nonlinearly with twist angle, preventing a smooth correlation between e_{33} and twist angle.