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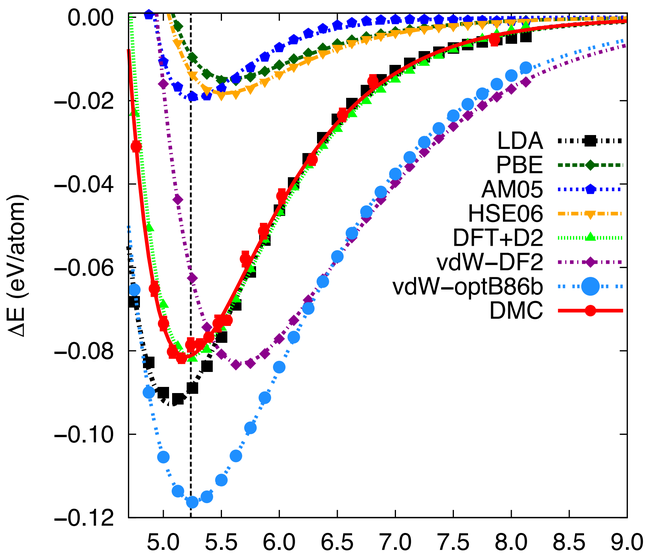
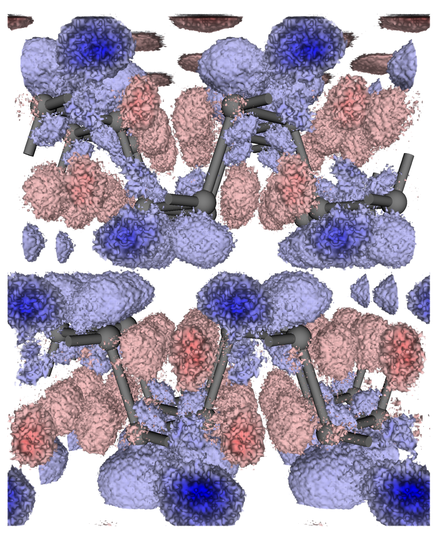
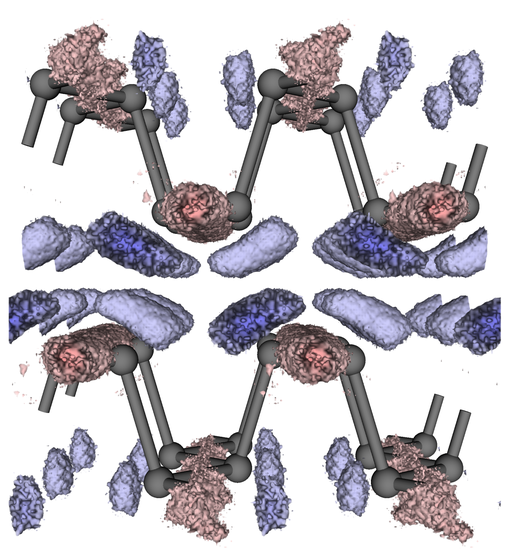
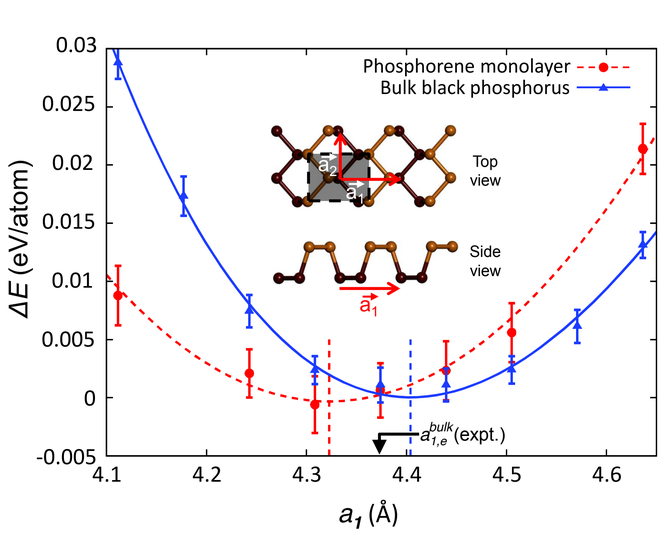






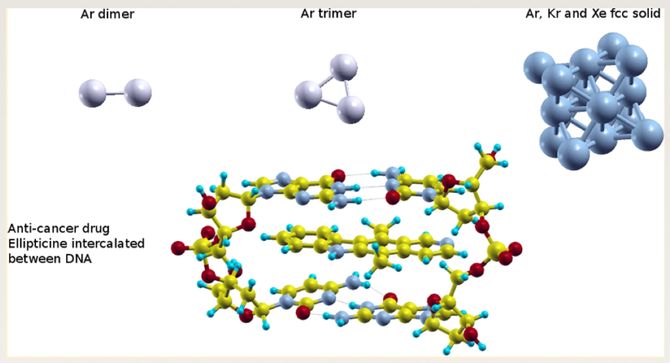


Is few-layer phosphorene a true van der Waals material?

L. Shulenburger[1], Andrew D. Baczewski[1], Jie Guan[2], Zhen Zhu[2] and David Tomanek[2]
[1]Sandia National Laboratories, Albuquerque, NM 87185, USA
[2]Physics and Astronomy Dept., Michigan State University, East Lansing, Michigan 48824, USA

Interlayer bonding in black phosphorus is mediated by dispersion interactions

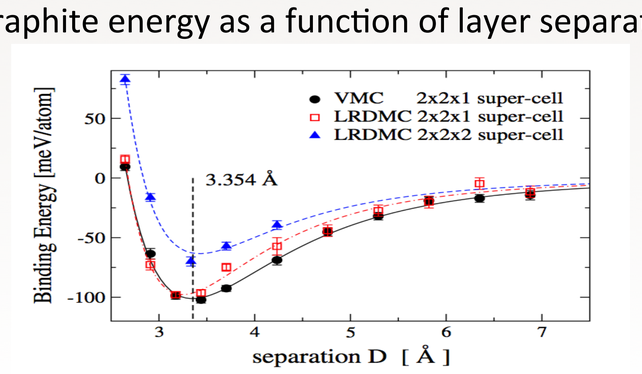
- Interactions within layers are covalent
- Interlayer binding is thought to be mediated by van der Waals forces
- Van der Waals interactions difficult to treat consistently within DFT
- Diffusion Monte Carlo (DMC) an ideal method for benchmarking interactions in such systems
- DMC does not have an approximate interaction like DFT and scales better than high level quantum chemistry



Benali, Shulenburger, Romero, Kim, von Lilienfeld, JCTC, 10, 3417 (2014)

- DMC has previously been successfully applied to graphite

Graphite energy as a function of layer separation

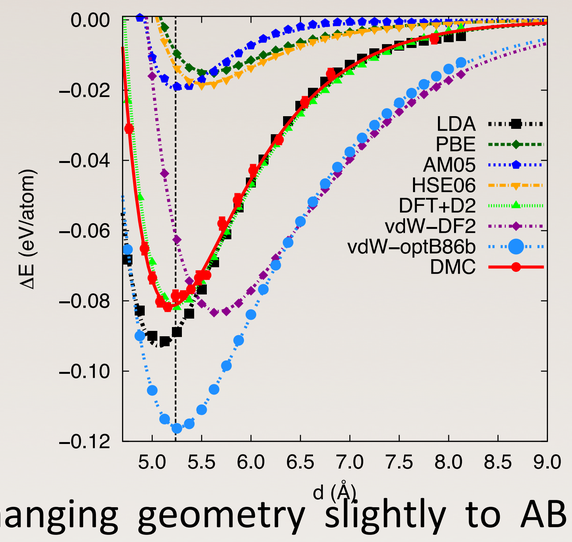


Spanu et al. PRL, **103**, 196401 (2009)

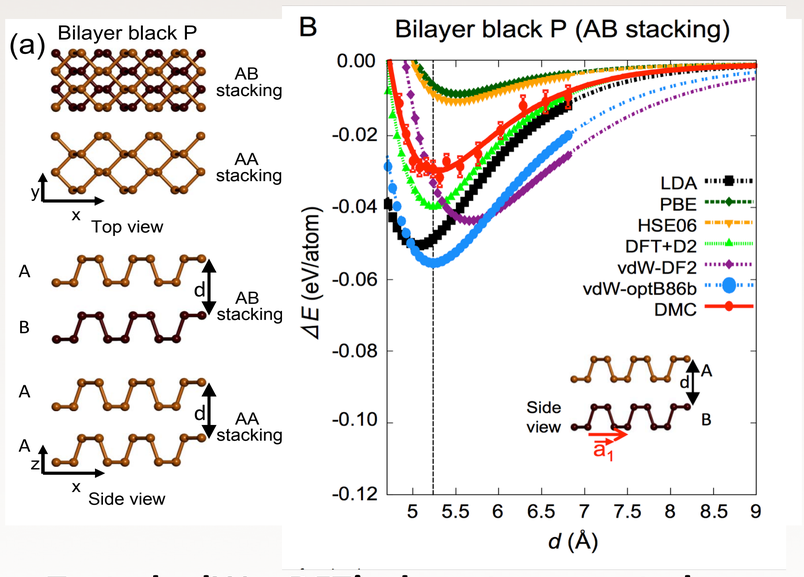
Benchmarking the interlayer interaction in black phosphorus shows deficiencies in DFT functionals

- Calculations of the interlayer spacing for black phosphorus show promising results for approximate DFT+D2

Energy vs layer spacing for black phosphorus



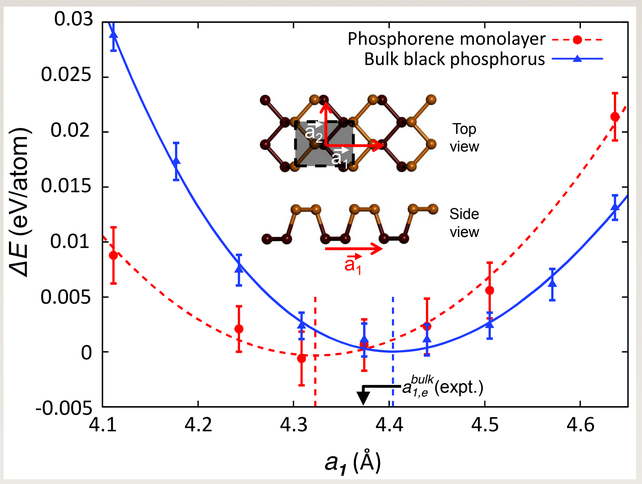
- Changing geometry slightly to AB bilayer changes relative performance of DFT functionals



- **Tested vdW + DFT's do not appear to be universal**
- Cleavage energy is 22.4±1.6 meV/Å^2 with exfoliation energy slightly smaller

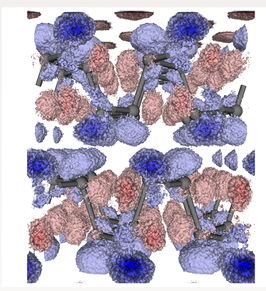
Interlayer interactions result in charge reorganization that is not captured well by current DFT functionals

- Comparing the in plane geometry of phosphorene and black phosphorus suggests that the interlayer interaction causes changes in the bonding

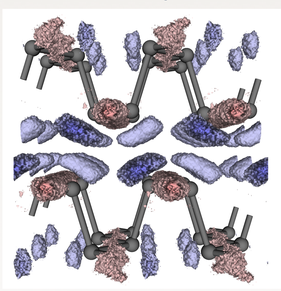


- Within DMC, the charge density difference between isolated phosphorene and bulk or bilayers shows charge depletion between layers and reorganization into bonds

Bulk

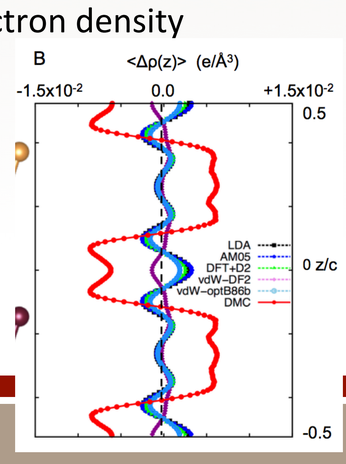


Bilayer



Red is area of increased electron density, blue decreased electron density

- Self consistent DFT functionals do not properly capture this mixed steric and van der Waals interaction



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