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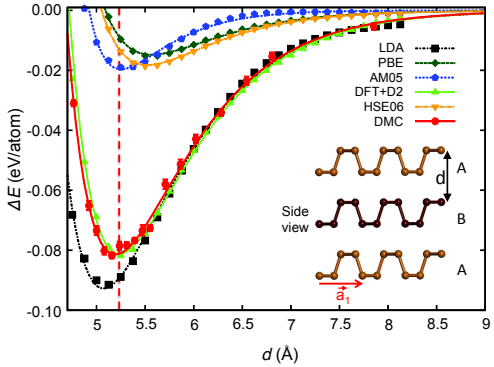

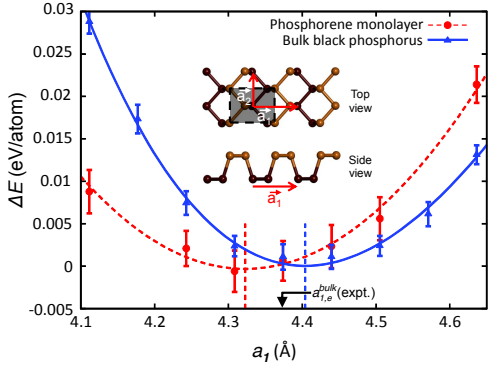

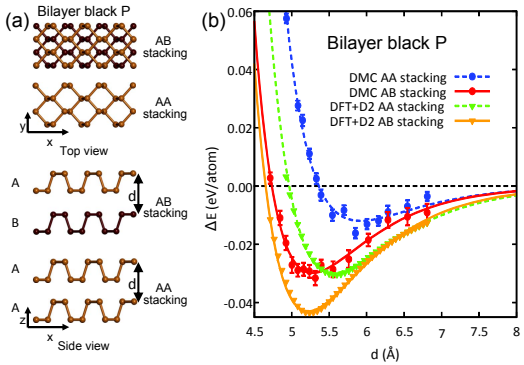

Quantum Monte Carlo Studies of Bulk and Few- or Single-Layer Black Phosphorus

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U.S. DEPARTMENT OF ENERGY
National Nuclear Security Administration

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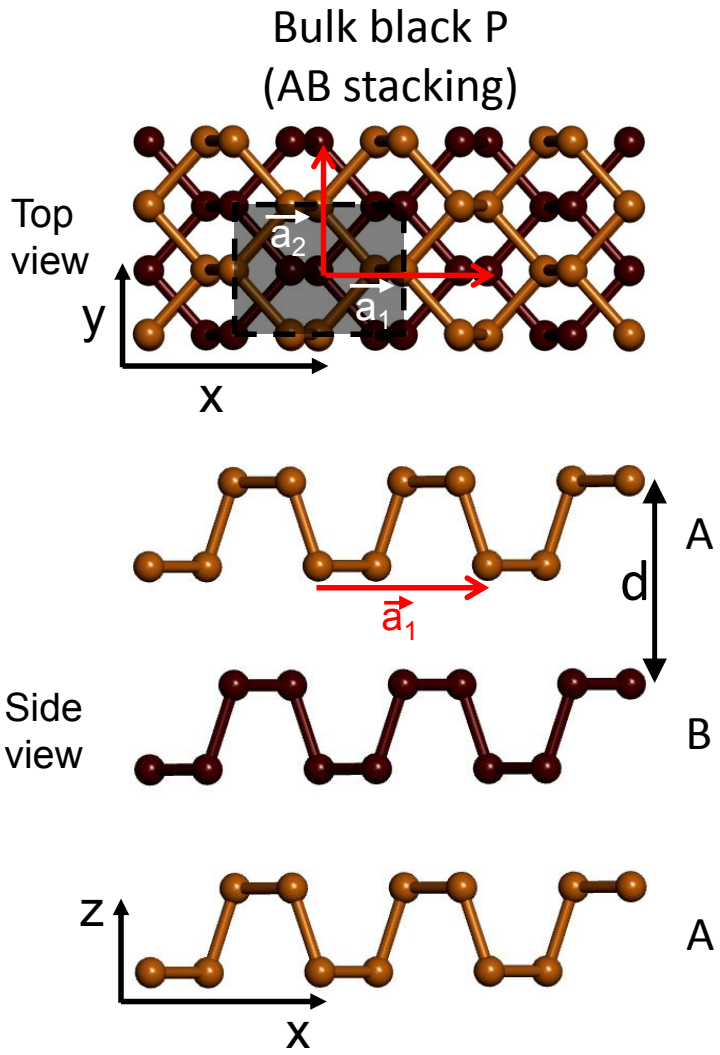
Electronic structure of phosphorus

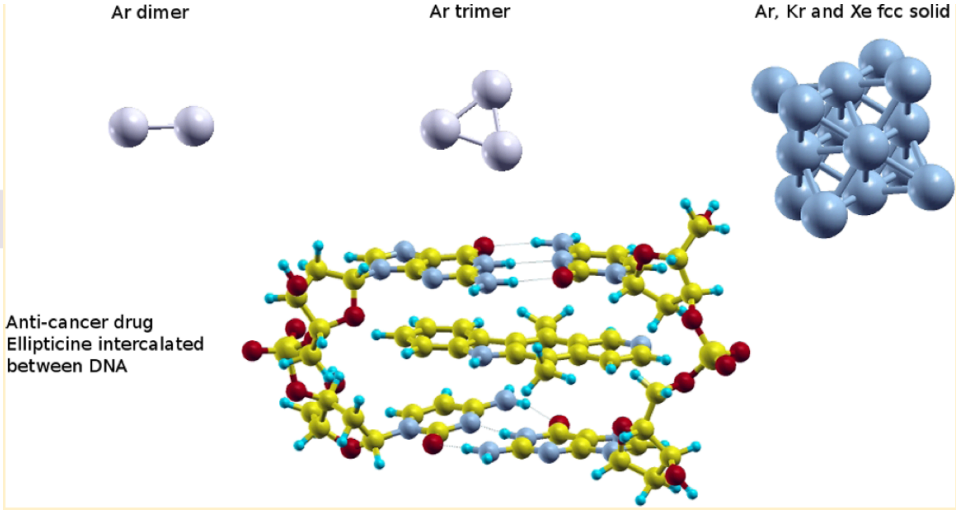


- Black phosphorus is a layered material
- Interactions within layers are covalent
- Transport is strongly anisotropic
- Interlayer binding is thought to be mediated by van der Waals forces
- Van der Waals interactions difficult to treat consistently within DFT

Diffusion Monte Carlo has been validated for large van der Waals systems

- Van der Waals interactions are handled naturally because the interaction is not approximated
- The scalability of the method allows calculations on hundreds of atoms

level of theory	ΔE_{bind}
DFT(PBE)	+5.2
DFT+C_6	−46.9[a]
DFT+C_6+C_9	−37.0[a]
DFT+TBD	−39.1[b]
DFT+MBD	−50.7[b]
DFT+MBDr	−35.4[c]
DFT+DCACP	−37.0[d]
DMC	−33.6 ± 0.9



Benali et al. JCTC, 2014

Previous work on graphite shows strengths and limitations of QMC for layered materials

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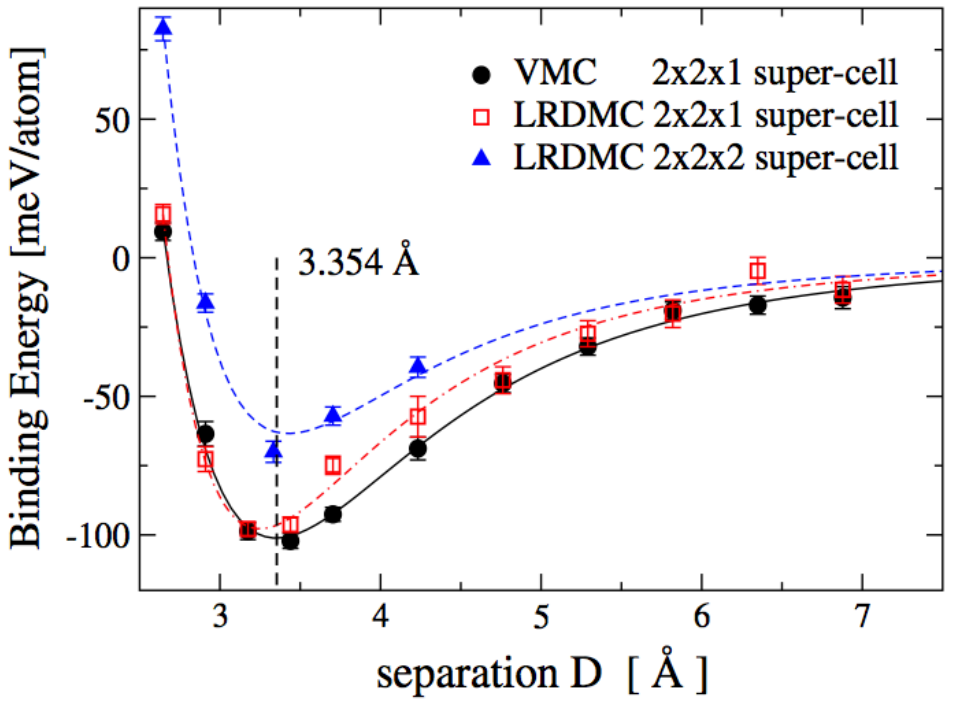
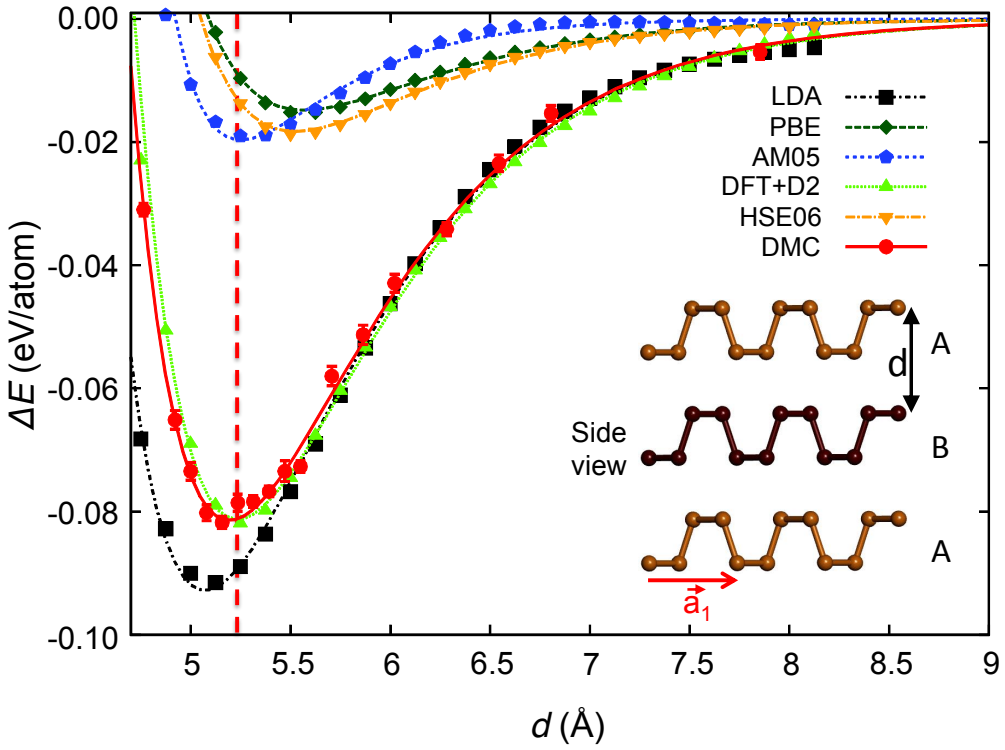
- Bond length is insensitive to calculation cell
- Difficulty developing a rigorous procedure for estimation of finite size effects makes energetics difficult
- Recent work extends to intercalation of lithium between graphite
  - P. Ganesh et al. JCTC, **10**, 5318 (2014)

Graphite energy as a function of layer separation



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

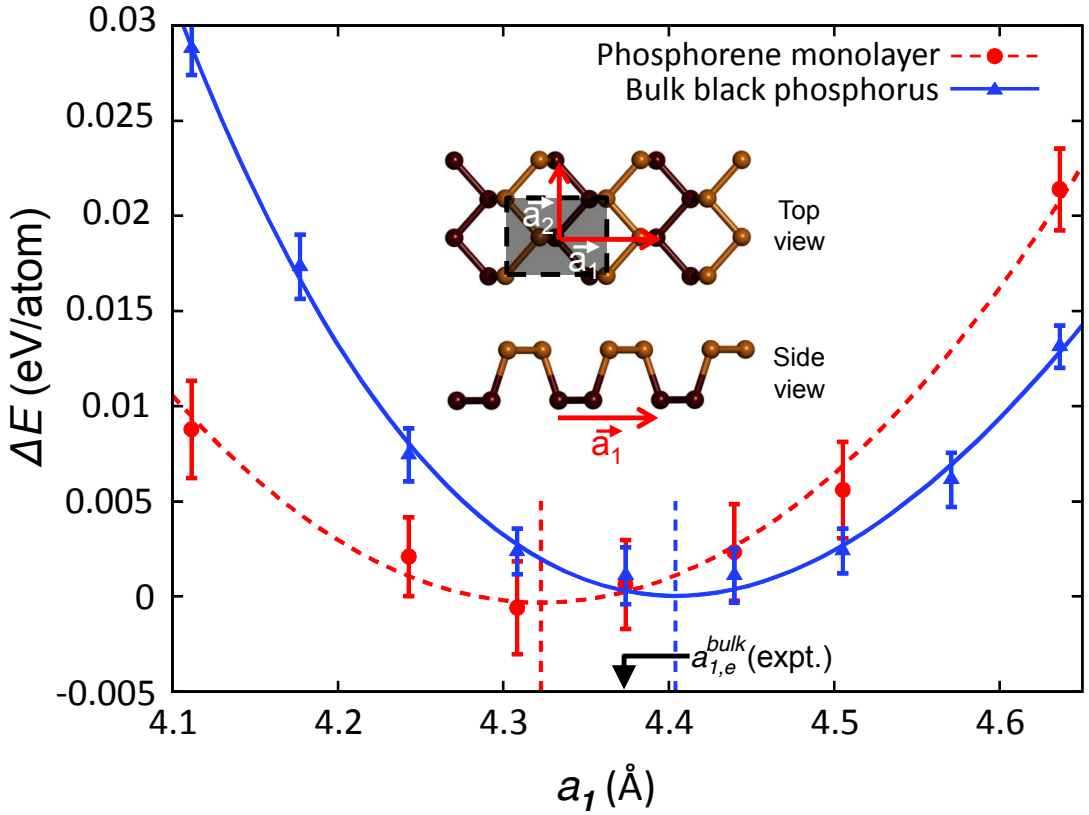
Calculations on bulk black phosphorus yield good structure compared to experiment



- Cannot easily calculate forces in DMC, using intralayer geometries from experiment
- Excellent agreement for interlayer separation between DMC and experiment
- DFT+D2 also shows excellent performance for both binding energy and geometry
- AM05 avoids spurious vdW interactions due to its construction, yet surprisingly the interlayer spacing is correct

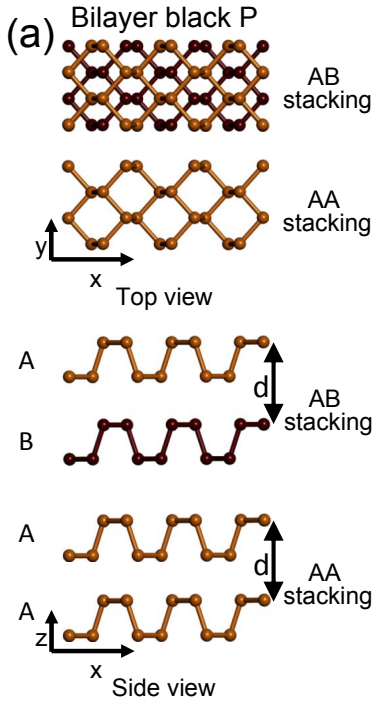
Intralayer geometry is sensitive to environment

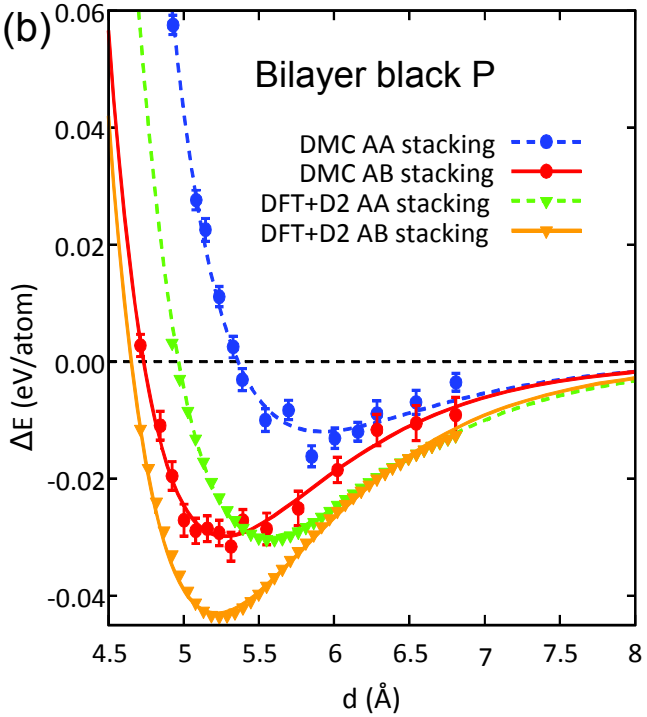
- Varying the intralayer geometry again yields a good agreement with the bulk black P experimental geometry
- The phosphorene monolayer is slightly contracted in the a_1 direction, suggesting rich effect of nearby layers on bonding



Varying the stacking of the a bilayer suggests steric effect

- Geometry within layers is frozen in bulk configuration
- AA stacked layers are much less strongly bound than AB
- Excellent agreement of DFT+D2 for bulk binding curve is not maintained
- Cleavage energy is 22.4±1.6 meV/Å^2 with exfoliation energy slightly smaller





Electron density shows significant rearrangement due to interaction

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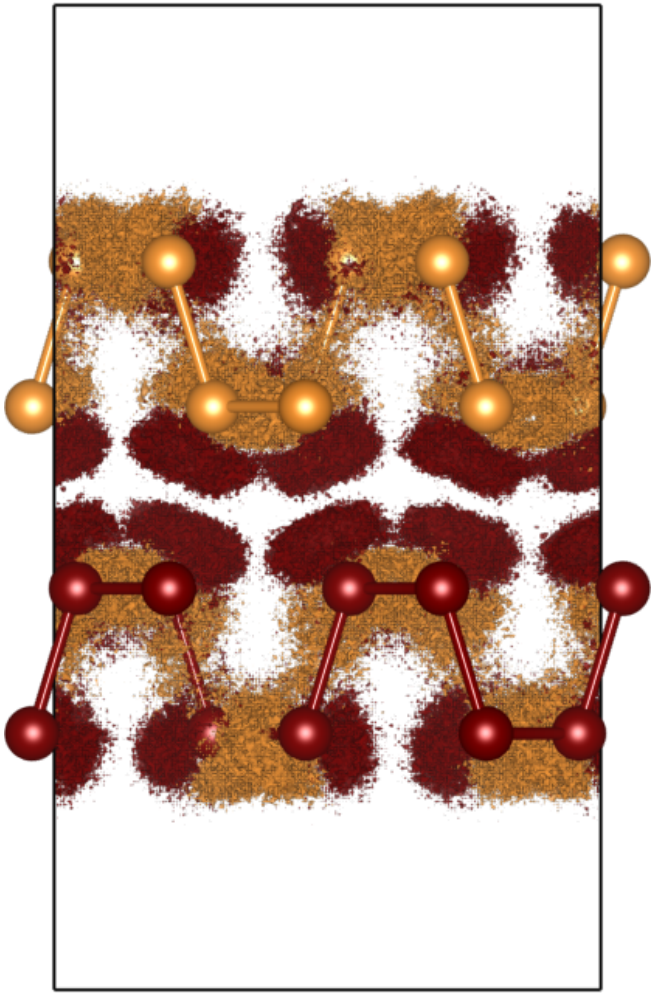
- For AB stacked bilayer, charge is depleted between the layers and redistributed into them
- Redistribution is significant, accounting for nearly 0.1 electrons / atom
- Pointwise C_6 corrections such as DFT+D2 will struggle to reproduce this character



DMC calculations reveal a complicated interlayer interaction for black phosphorus

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- Binding of phosphorene layers is significantly more complicated than a simple van der Waals interaction between slabs
- Intralayer interaction is affected by nearby layers
- Steric effects cause significant change in binding between AA and AB stacking
- Binding causes a significant redistribution of charge