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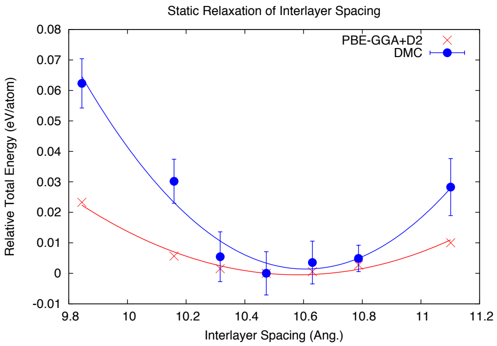

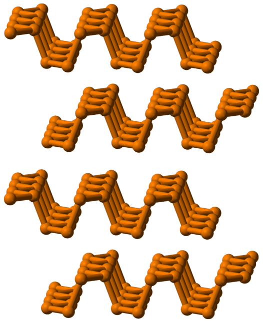

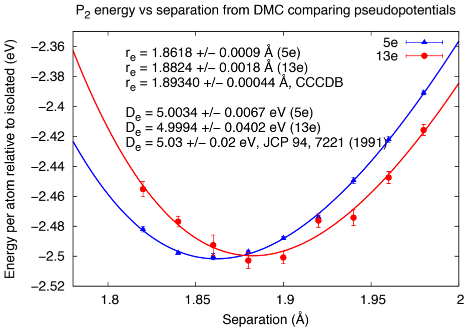

Quantum Monte Carlo Studies of Bulk and Few-/Single-Layer Allotropes of Phosphorus

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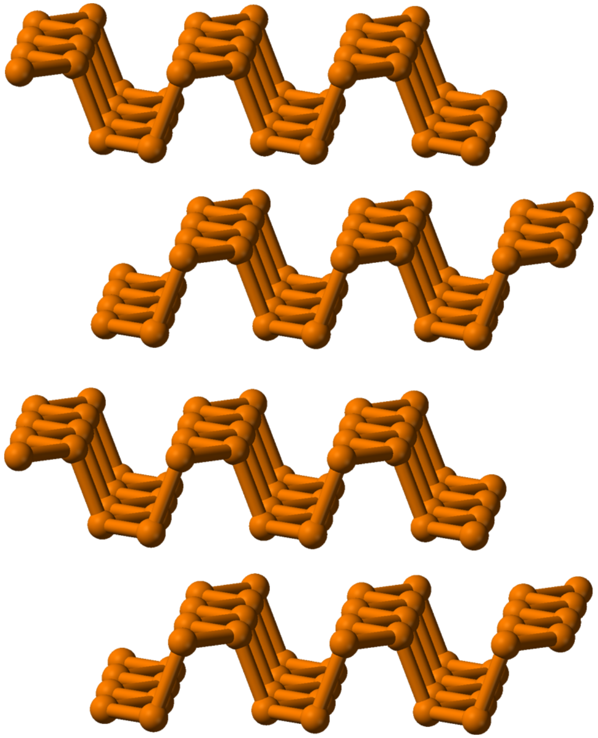
U.S. DEPARTMENT OF ENERGY NNSA National Nuclear Security Administration

Electronic structure of phosphorus

- Black phosphorus is a layered material
- Interactions within layers are covalent
- Interactions between layers are mediated by dispersion
- Transport occurs primarily within layers
- Environment of layers does affect transport
- It would be useful to be able to predict these properties from quantum calculations



Standard electronic structure approach – Density Functional Theory (DFT)

- Density functional theory
    - Replace 3N dimensional wavefunction with 3 dimensional density
    - Kinetic piece is approximated well by using an ansatz of a noninteracting problem in an effective potential
    - Challenge is to replace simple Coulomb interaction with effective potential
        - Classes of approximation vary in what information is included

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  - Challenge is to replace simple Coulomb interaction with effective potential
    - Classes of approximation vary in what information is included
      - Local density only
      - Gradients of density
      - Local kinetic energy density
      - Global density
      - Noninteracting wavefunction
    - Approximations are non-perturbative

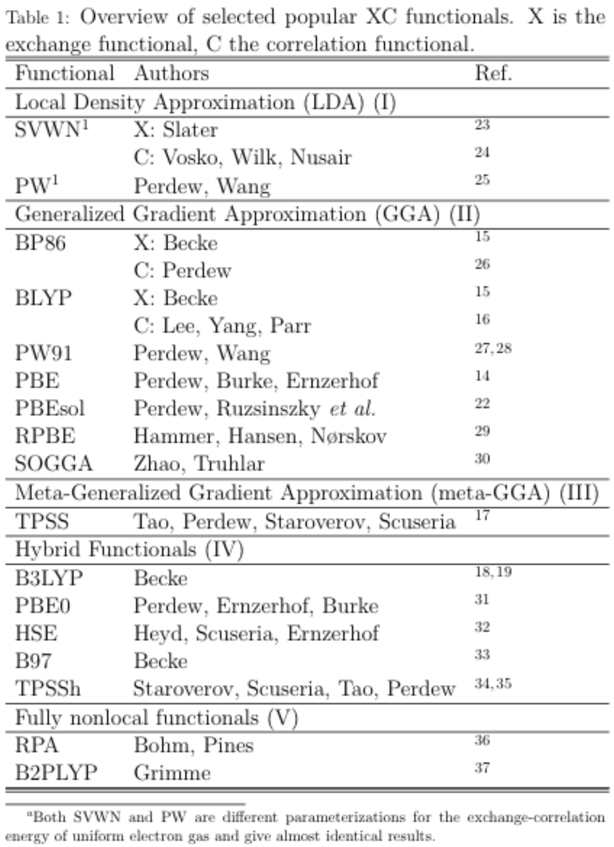


Table 1: Overview of selected popular XC functionals. X is the exchange functional, C the correlation functional.

Functional	Authors	Ref.
Local Density Approximation (LDA) (I)		
SVWN[1]	X: Slater	23
	C: Vosko, Wilk, Nusair	24
PW[1]	Perdew, Wang	25
Generalized Gradient Approximation (GGA) (II)		
BP86	X: Becke	15
	C: Perdew	26
BLYP	X: Becke	15
	C: Lee, Yang, Parr	16
PW91	Perdew, Wang	27, 28
PBE	Perdew, Burke, Ernzerhof	14
PBEsol	Perdew, Ruzsinszky *et al.*	22
RPBE	Hammer, Hansen, Nørskov	29
SOGGA	Zhao, Truhlar	30
Meta-Generalized Gradient Approximation (meta-GGA) (III)		
TPSS	Tao, Perdew, Staroverov, Scuseria	17
Hybrid Functionals (IV)		
B3LYP	Becke	18, 19
PBE0	Perdew, Ernzerhof, Burke	31
HSE	Heyd, Scuseria, Ernzerhof	32
B97	Becke	33
TPSSh	Staroverov, Scuseria, Tao, Perdew	34, 35
Fully nonlocal functionals (V)		
RPA	Bohm, Pines	36
B2PLYP	Grimme	37

[a] Both SVWN and PW are different parameterizations for the exchange-correlation energy of uniform electron gas and give almost identical results.

Improving electronic approximations:

Quantum Monte Carlo

- Solve Schrodinger equation directly?

$$i\hbar \frac{\partial}{\partial t}\Psi(t,r_1\ldots r_N) = \hat{H}\Psi(t,r_1\ldots r_N)$$

$$\hat{H} = -\sum_i \frac{\nabla_i^2}{2m} + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{\left|\vec{r}_i - \vec{r}_j\right|} + \sum_{i,I}\frac{Z_I e^2}{\left|\vec{R}_I - \vec{r}_i\right|} = \hat{T} + \hat{V}$$

- Ignore scaling problem
  - Green’s function approach changes differential equation to integral
- Integral is still evaluated in 3N dimensions!
  - Stochastic sampling vs deterministic

Error ∝ $N^{-1/D}$

Error ∝ $1/\sqrt{N}$

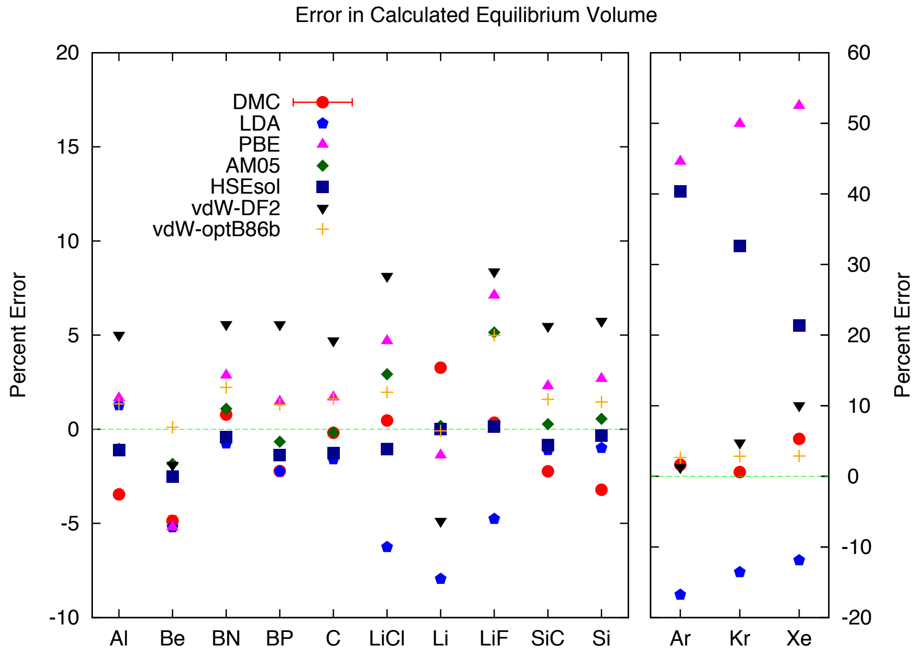
Circle area
~ 6/7 of
square

Stochastic Sampling + Schrodinger Equation = Quantum Monte Carlo

- Integral still exists in a very large space
  - Guide sampling according to trial wavefunction from another method
    - Often DFT wavefunction X correlation terms
  - Still exact as long as guess satisfies certain properties
- Must recast integrand as a probability distribution
  - Probability distributions must be positive everywhere
  - Wavefunction is not positive definite!
  - Restrict sampling using nodes of trial wavefunction
- This advance allowed the calculation of the energy of the homogeneous electron gas
  - Basis for all DFT calculations
  - Ceperley and Alder. PRL. **45**, 566–569 (1980)

Accuracy in solids has been shown to be equal to or better than DFT on a large class of solids

- **Fit Vinet form to E(V) and compare equilibrium volume (density) and bulk modulus of solids (compressibility) to experiment**

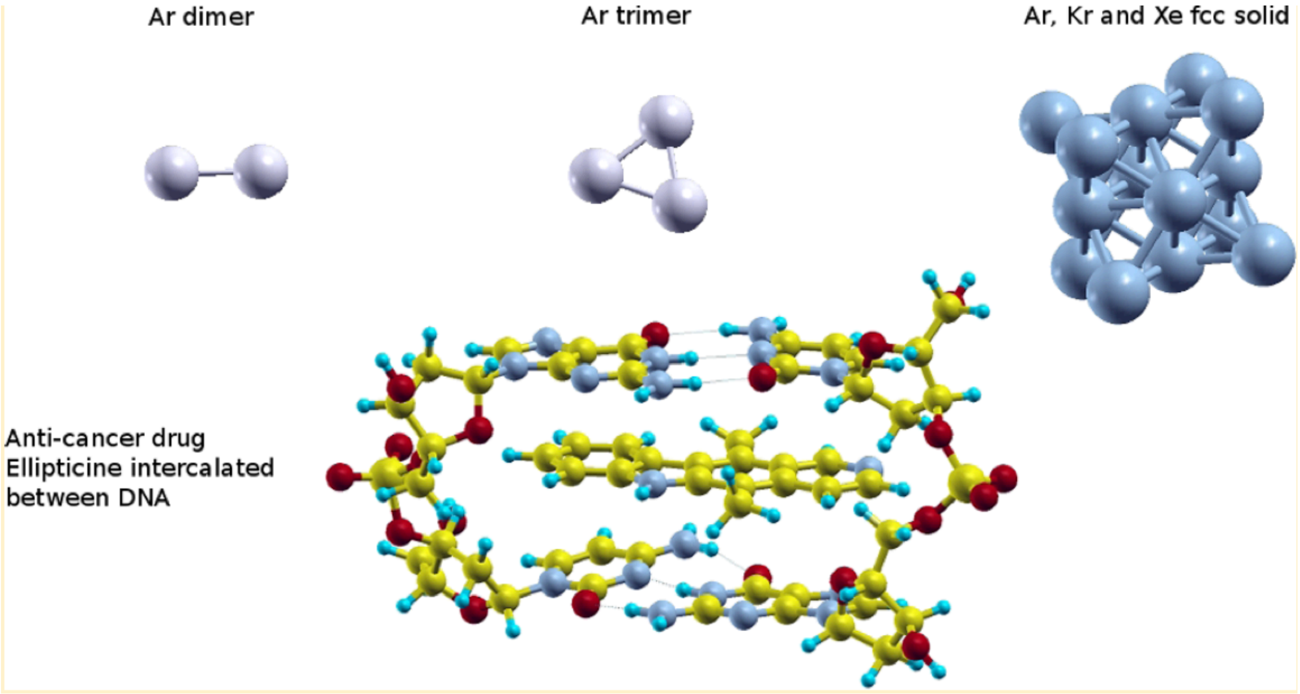


- Materials span a factor of 10 in equilibrium volume
- Four types of bonding are included
  - Ionic
  - Covalent
  - Metallic
  - Van der Waals
- Lattice Constants within ~0.9%
- Accuracy comparable to popular DFT functionals of many different types
- PRB 88, 245117 (2013)

Mean error: -0.38 +/- 0.15
Mean absolute error: 2.28 +/- 0.15
RMS error: -0.697 +/- 0.066%
Mean absolute relative error: 1.79 +/- 0.07%

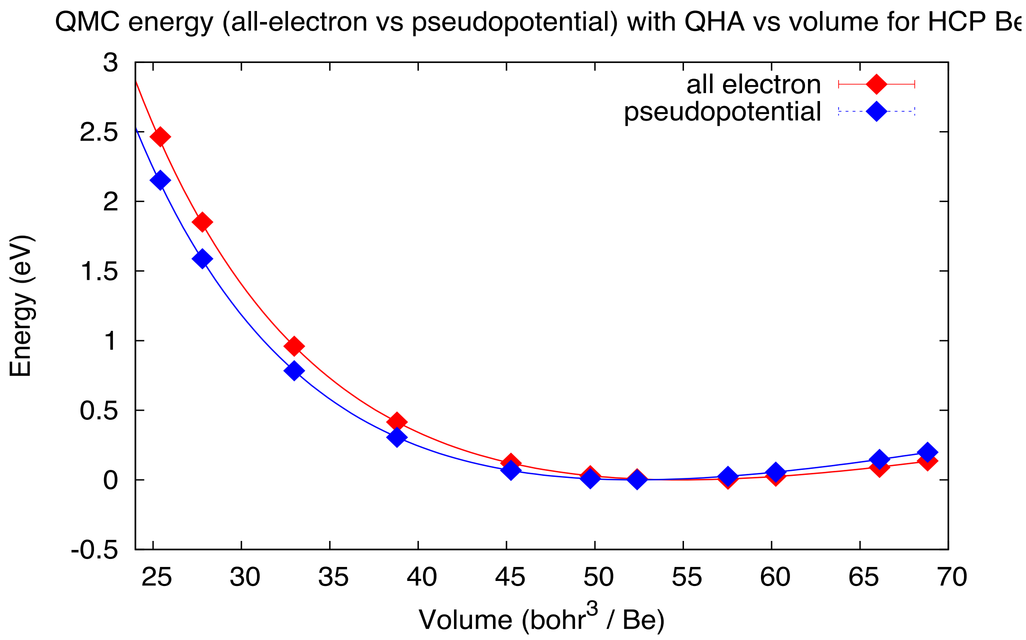
The method has been validated for large van der Waals systems

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



Benali et al. JCTC, 2014

The largest approximation is often the core-valence partitioning (pseudopotentials)



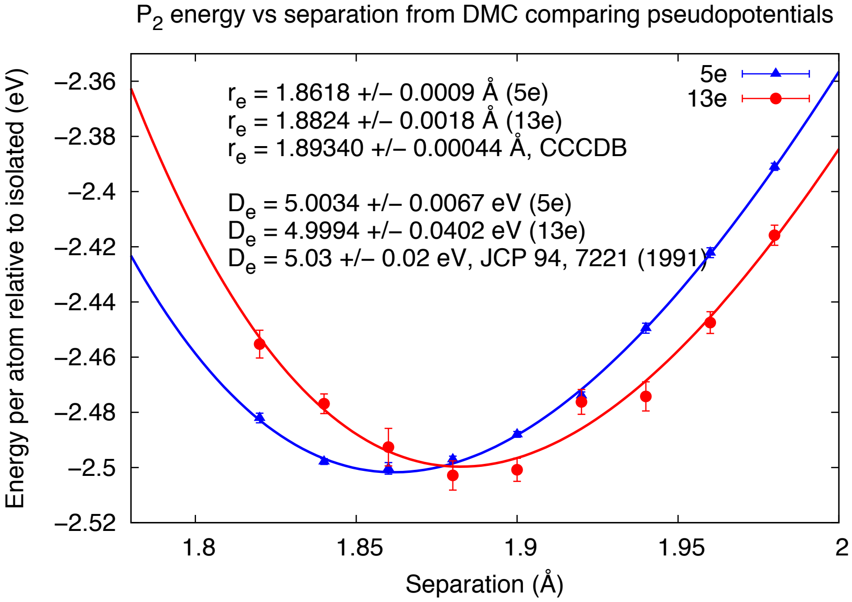
- Be is a case where the performance was poor relative to DFT
- Compare all electron calculations to pseudopotential ones
- All electron EOS Properties agree with experiment within small error bars!

HCP Equilibrium Parameters

	QMC	All Electron QMC	Exp
c/a	1.569 +/- 0.004	1.569 +/- 0.004	1.568
V_0 (angstrom^3)	7.746 +/- 0.078	8.129 +/- 0.012	8.117
Bulk Modulus (Gpa)	124 +/- 2	115.7 +/- 1.5	116.8

Two pseudopotentials were tested and validated for phosphorus

- **Compare properties of dimer and isolated atom to experiment**



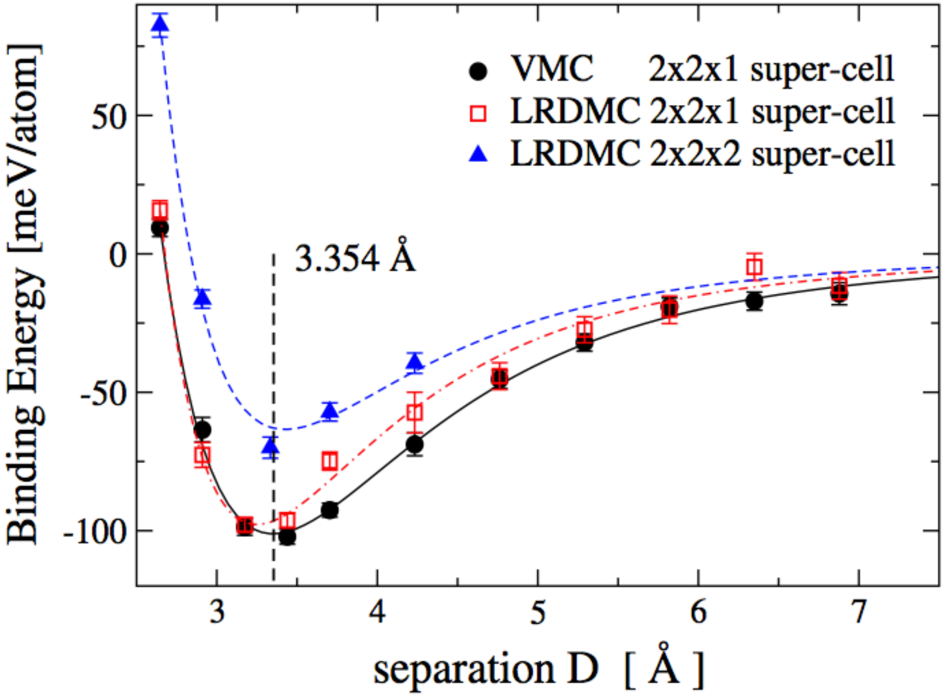
- Accuracy of atomic results is limited in practice by the choice of trial wavefunction
- Both choices of valence yield results in good agreement with experiment (within fixed node error)

	5 e^- valence	13 e^- valence	expt
Ionization potential	10.7112 +/- 0.00084	10.6832 +/- 0.0598	10.48669
Electron affinity	0.6405 +/- 0.0084	0.7483 +/- 0.0626	0.746609

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

- Bond length is insensitive to calculation cell
- Rigorous procedure for estimation of finite size effects makes energetics difficult

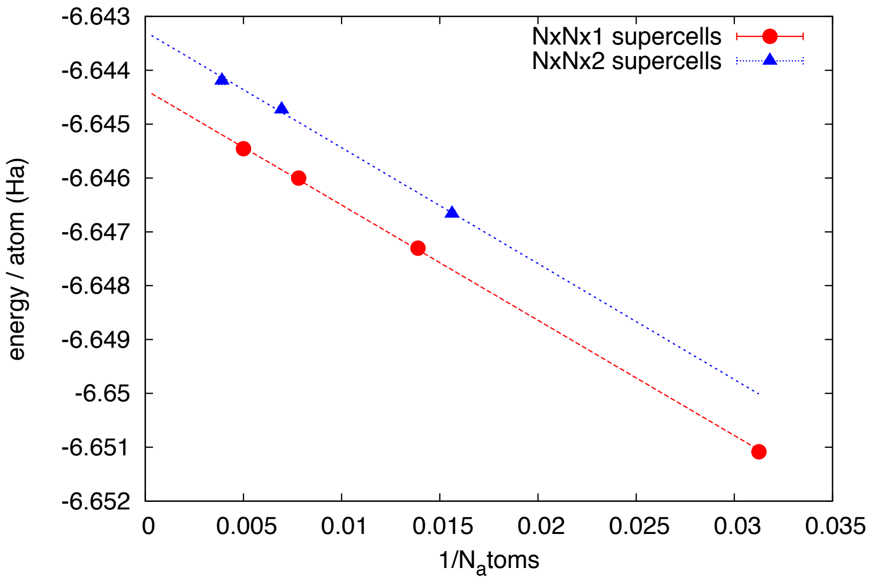
Graphite energy as a function of layer separation



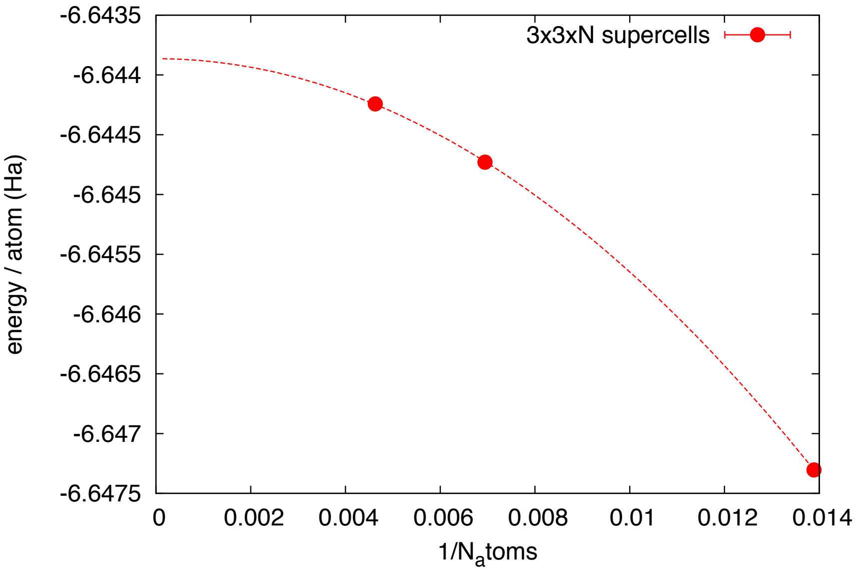
Spanu et al. PRL, **103**, 196401 (2009)

Advances in computational resources have allowed insight into finite size effects for layered materials

In plane is insensitive to number layers



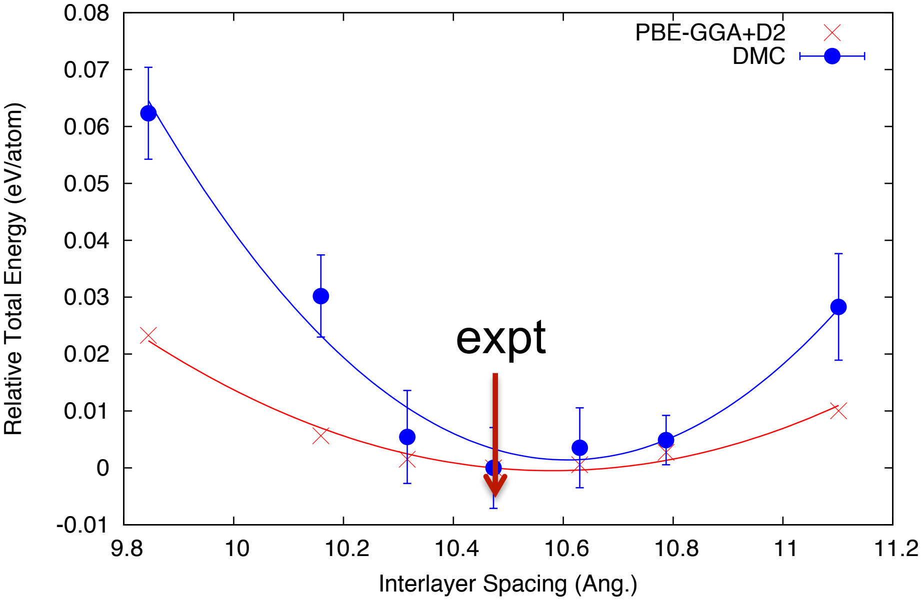
$1/N^2$ scaling with number of layers



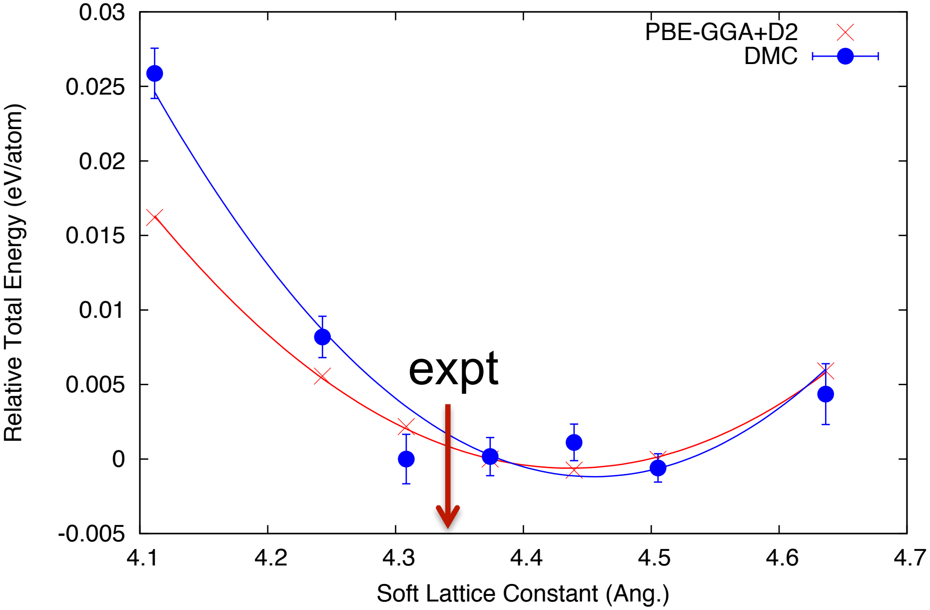
Calculations on bulk black phosphorus yield good structure compared to experiment

- Cannot calculate forces in DMC, using geometries from approximate DFT vdW functional
- Considerably stiffer as a function of layer spacing than GGA+D2

Static Relaxation of Interlayer Spacing

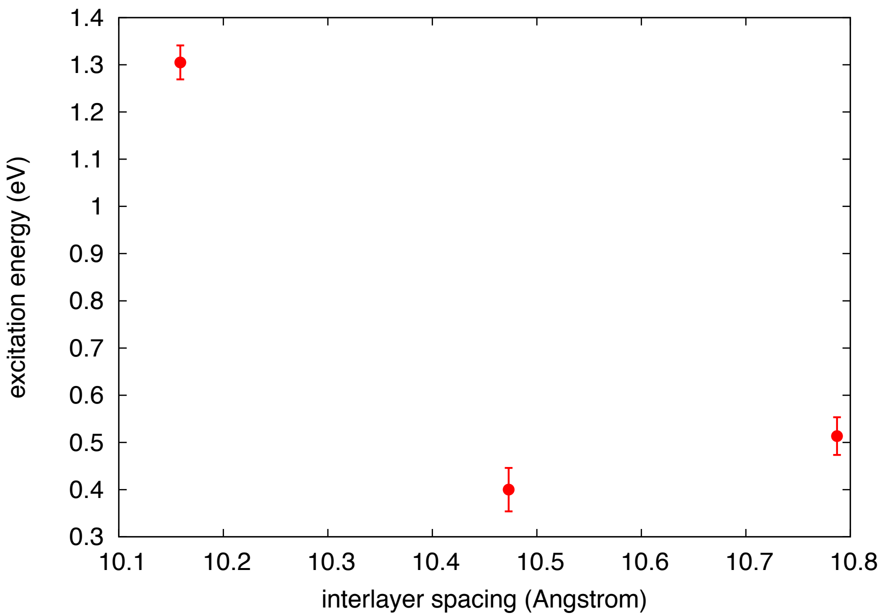


Static Relaxation of Soft Axis



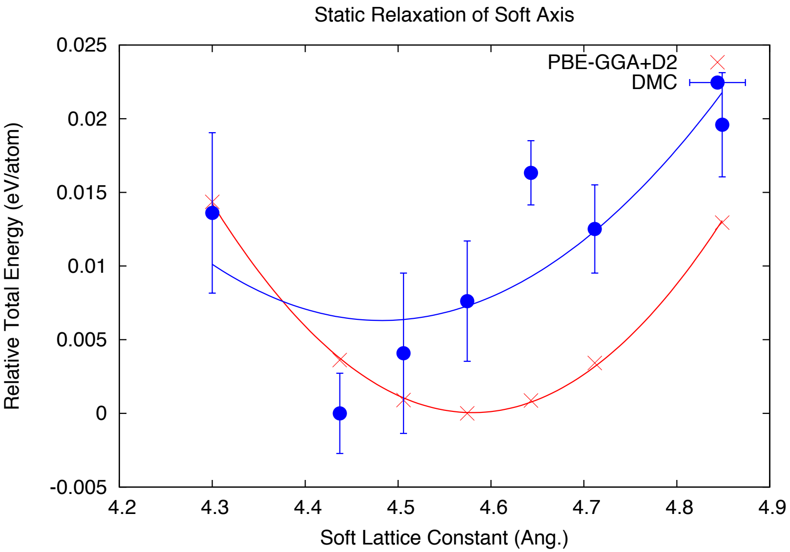
Calculations of bound exciton show strong influence of layer spacing

- Calculations performed by exciting an electron to the conduction band in the DMC trial wavefunction (provides upper bound on true excitation energy)
- Good agreement with experiment at equilibrium geometry

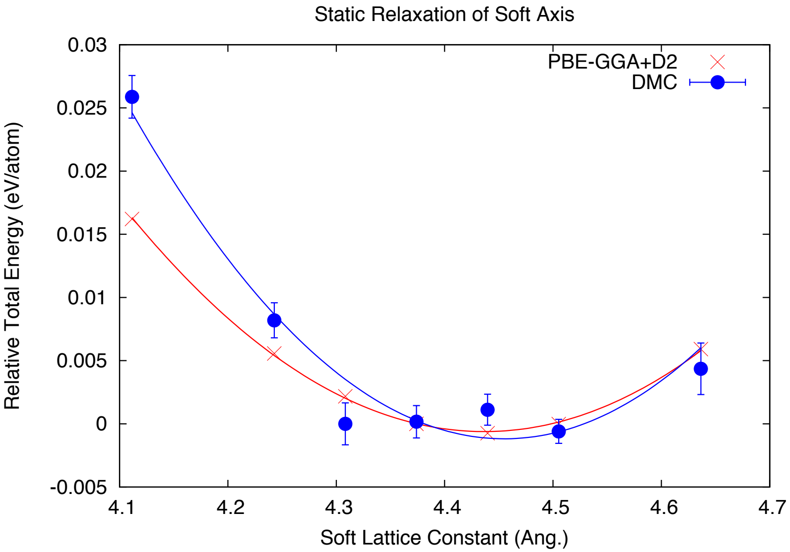


Isolated black phosphorene shows little relaxation of geometry from bulk

Single layer



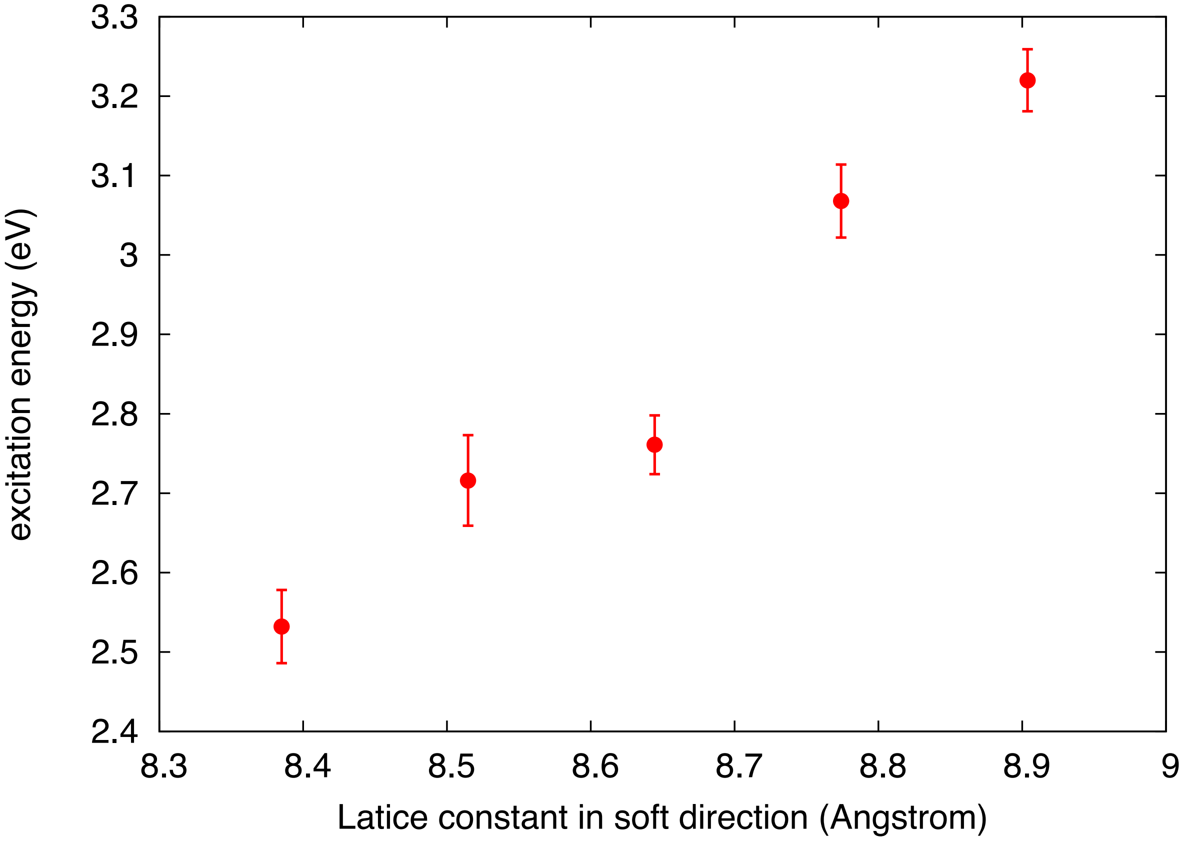
Bulk



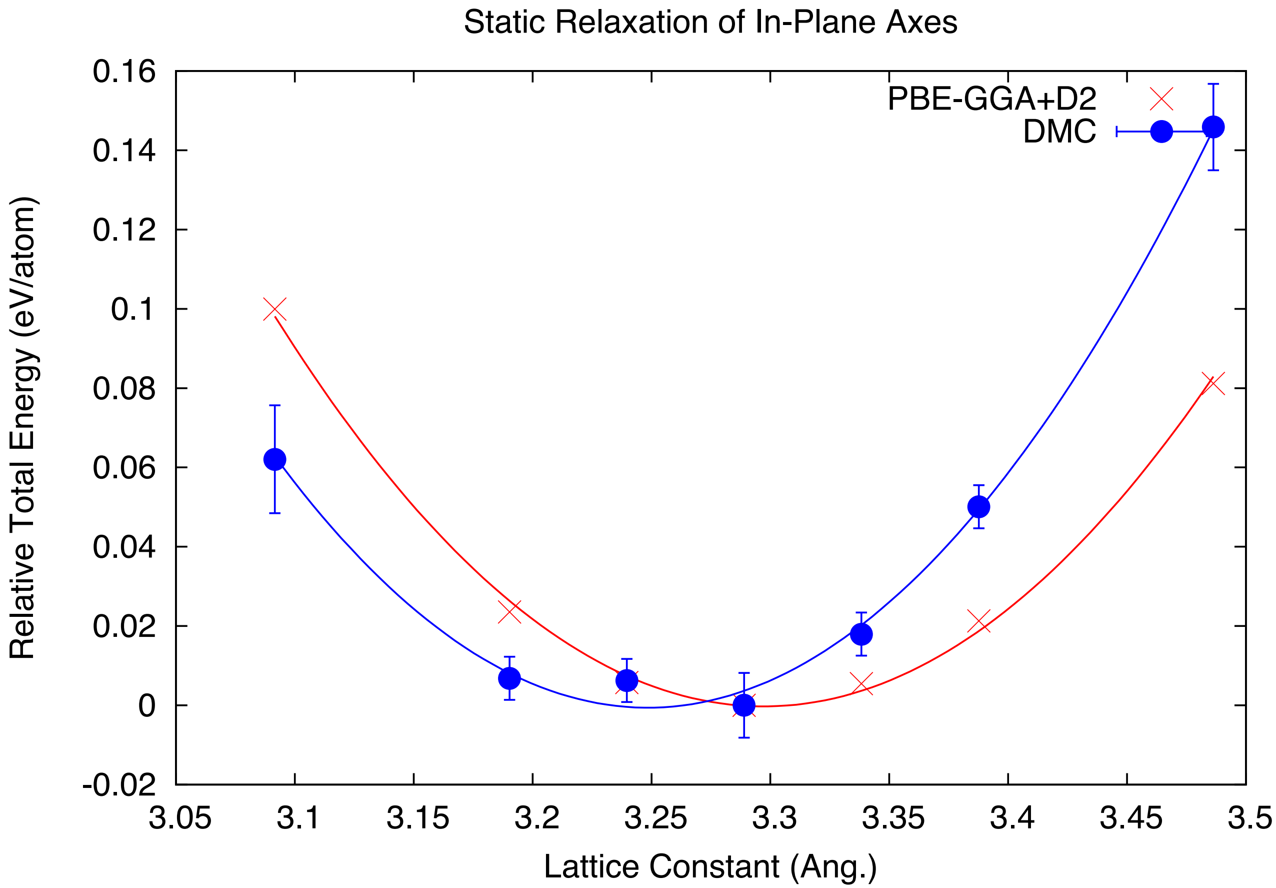
Allows calculation of binding energy wrt layer spacing: 40 +/- 7 meV

Optical excitation for phosphorene shows linear increase with strain

- Values considerably larger than experiment
  - Role of environment?
  - Trial wavefunctions from DFT possibly worse?



Blue allotrope is similarly underbound by DFT within the sheet



Conclusions

- Electronic structure of phosphorus is challenging for DFT
- DMC provides an alternative with proven accuracy for vdW, but challenges for layered materials
- DMC results for black phosphorus provide excellent geometries compared to experiment
- Comparison with single layer sheet provides binding energy of 40 +/- 7 meV
- Calculations of optical properties a work in progress but suggest DFT wavefunctions are significantly better for bulk than layered structure