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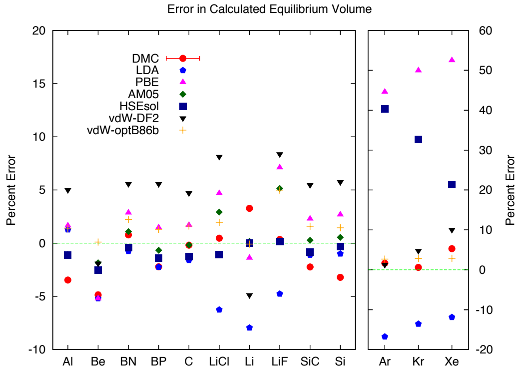
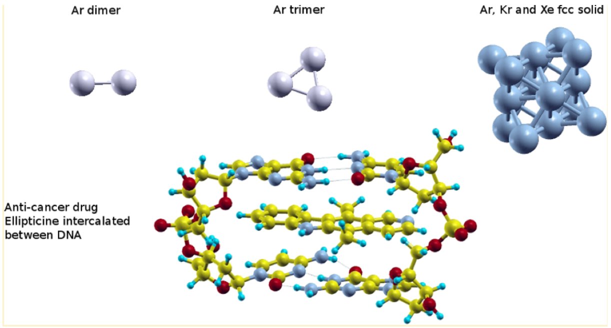
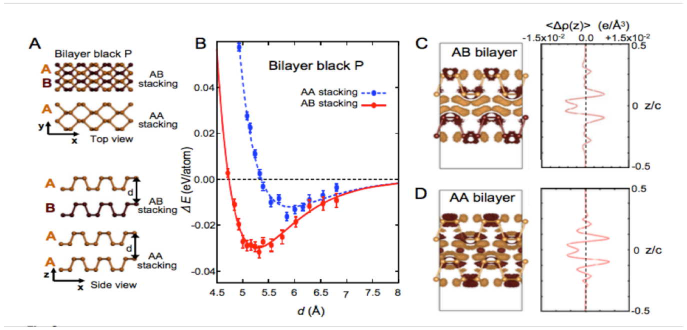






Exploring the promise of diffusion Monte Carlo for materials research

Luke Shulenburger

U.S. DEPARTMENT OF ENERGY

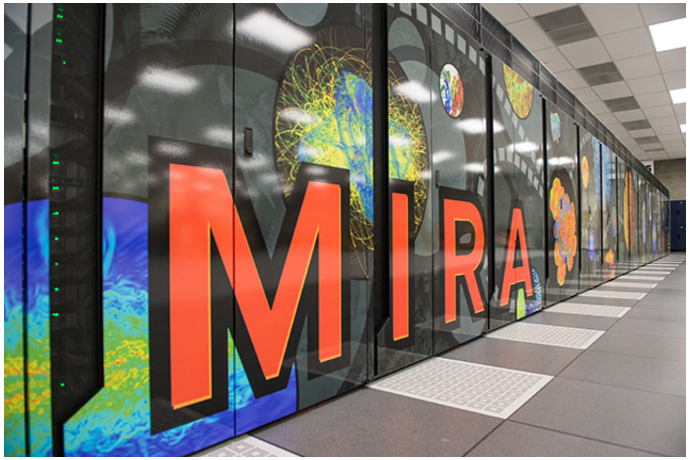
NNSA National Nuclear Security Administration

Collaborations

- Numerous collaborators through BES “Network for ab initio many-body methods: development, education & training”
  - Anouar Benali, Jeff Greeley, Nichols Romero and Ye Luo at ANL
- Sandia National Laboratories
  - Thomas Mattsson and Mike Desjarlais
- Strongly Correlated Oxides
  - Olle Heinonen and ANL and Ron Cohen at Carnegie Institution of Washington
- Layered Materials
  - David Tomanek, Zhen Zhu and Jie Guan at MSU
- Van der Waals Compounds
  - Anatole von Lilienfeld at Basel, Miguel Morales, Ray Clay and Randy Hood at LLNL

Computing time

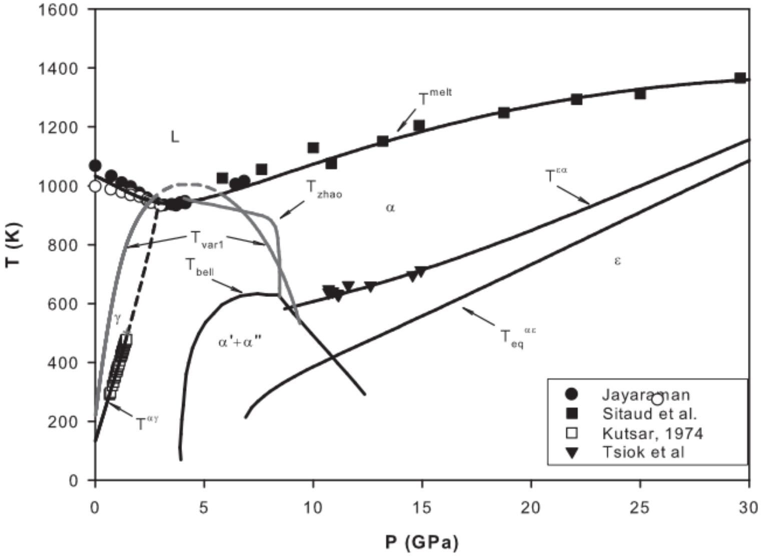
- INCITE
- ASC



Goal is to understand properties of a wide variety of materials

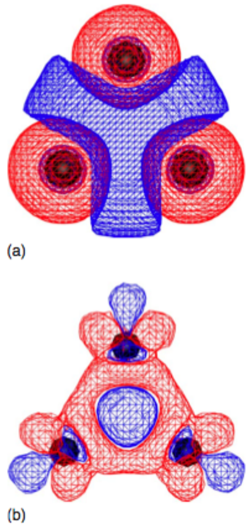
- Van der Waals interactions
- Localization vs delocalization
- Kondo physics
- Charge transfer
- Chemical Reactions

Cerium Phase diagram



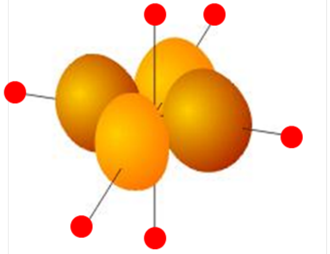
Elkin et al. PRB 84, 094120 (2011)

Xe isosurfaces



Tkatchenko et al PRB **78**, 045116 (2008)

Localized d-orbital in FeO



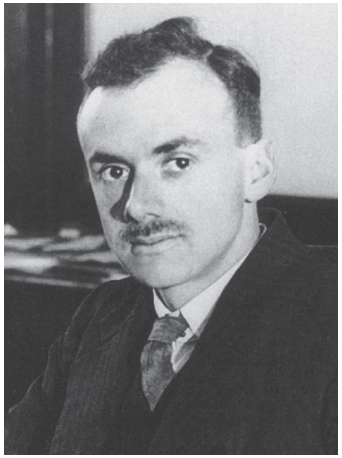
e_g orbital with surrounding oxygen ions

Towards ab initio simulation of materials

- Goal: Solution of governing equations without approximation
  - Equations are the same for carbon at 50 Mbar and dilute xenon gas
  - Results would be predictive for all materials and environments!

"The underlying physical laws necessary for a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact applications of these laws lead to equations much too complicated to be soluble."

-- Paul Dirac 1929



Confronting the abyss

- Can write the equations but cannot hope to solve them exactly:

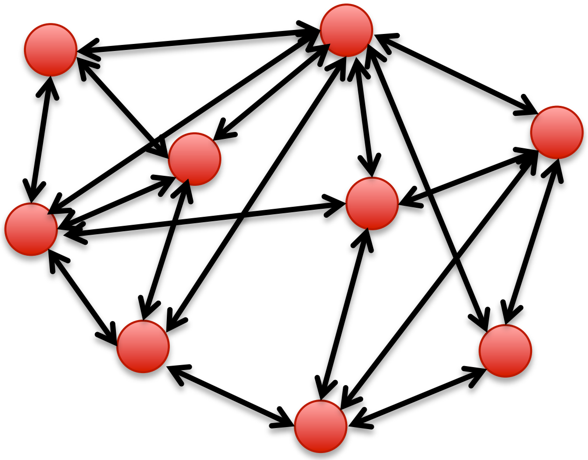
$$\hat{H}\Psi(r_1 \ldots r_N) = E\Psi(r_1 \ldots r_N)$$

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

  - 3N dimensional PDE with complicated boundary condition
  - To solve naïvely on a grid
    - 3 dimensions per electron
    - 20 points in each direction
    - $20^9 \approx 512$ billion points for 3 electrons
      - 3.6 TB just to store!
- Different approximations are common with tradeoffs

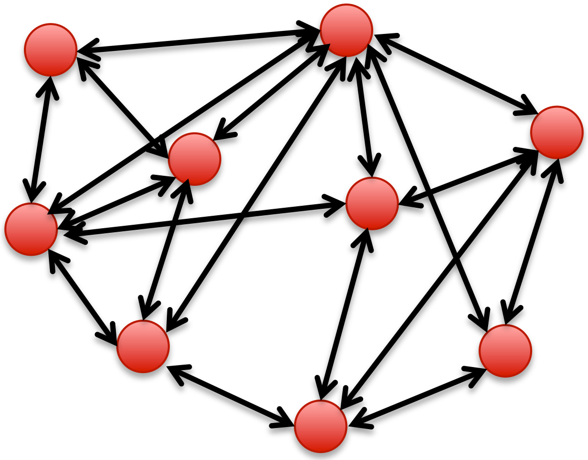
Parallel problem: Measuring capital flow

- Goal: model capital flow in the economy
- Strategy: Track all transactions



Electronic structure via econometrics

- Goal: model capital flow in the economy
- Strategy: Track all transactions
  - Strength – Exact Solution!
  - Weakness – Cost grows prohibitively with size of network analyzed
- Analogous to some quantum chemistry wavefunction based methods

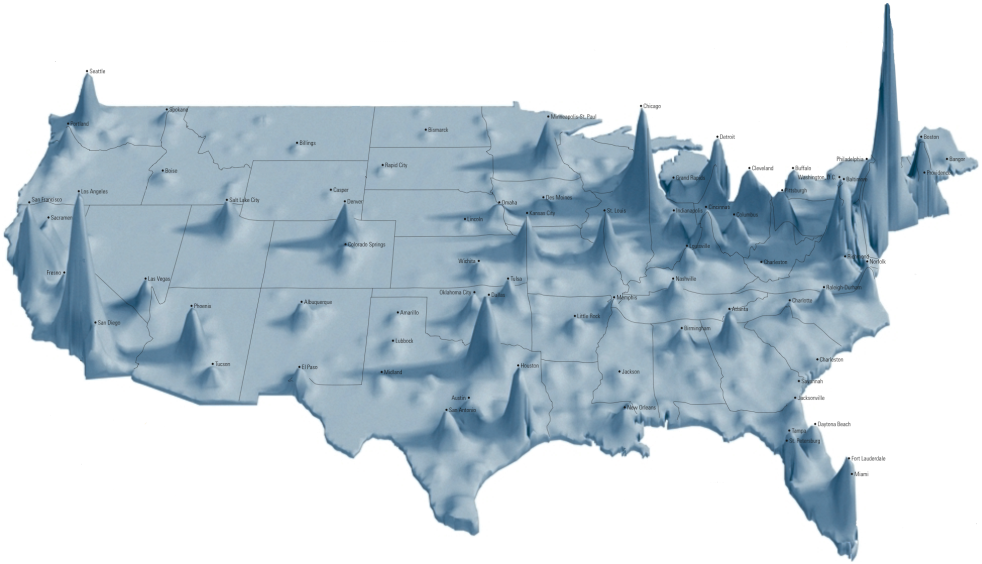


Economic problem $O(N^2)$
Electronic structure $O(N^7)$ – $O(N!)$

Parallel Problem: Measuring capital flow

- Strategy:
  - Study transactions in representative population densities
  - Map population density across the economy

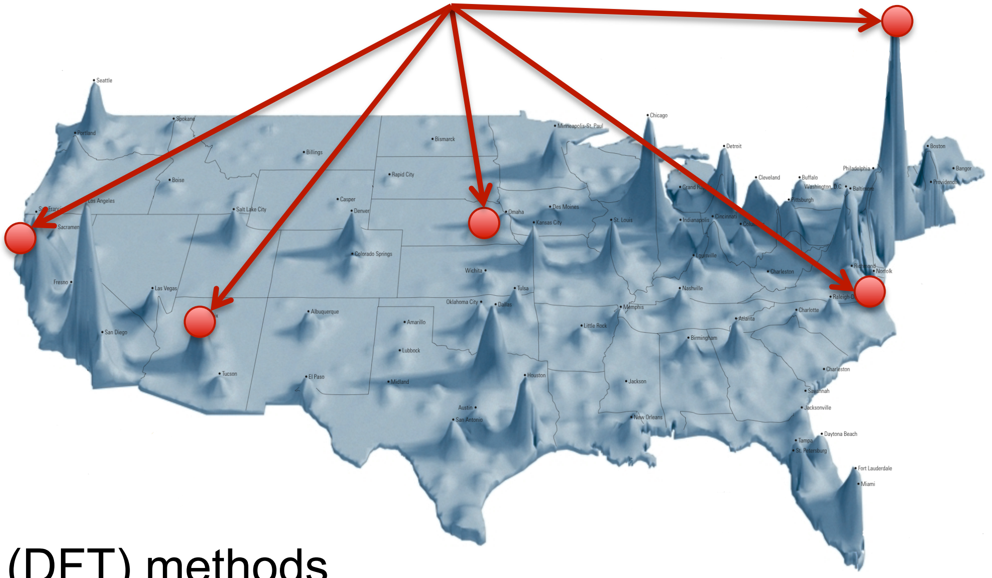
- Rural → Agriculturally dominated
- Suburban → Retail transactions, commuting
- Urban → corporate actors, real estate



Parallel Problem: Measuring capital flow

- Strategy:
    - Study transactions in representative population densities
    - Map population density across the economy

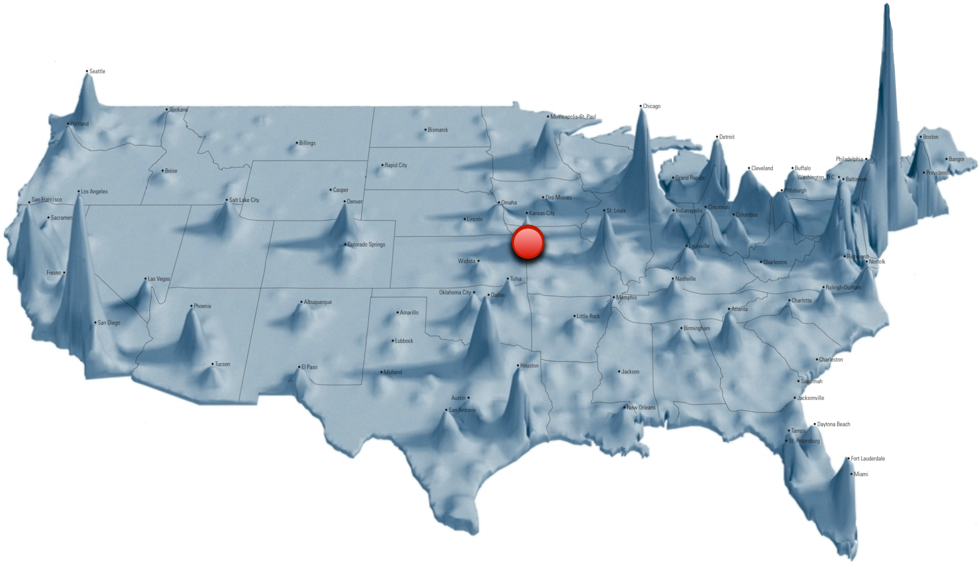
- Strength – Scales well to larger economies, accurate where model performs well
- Weakness – Difficulties with rare but important factors, difficult to improve model



Analogous to density functional theory (DFT) methods

Parallel Problem: Measuring capital flow

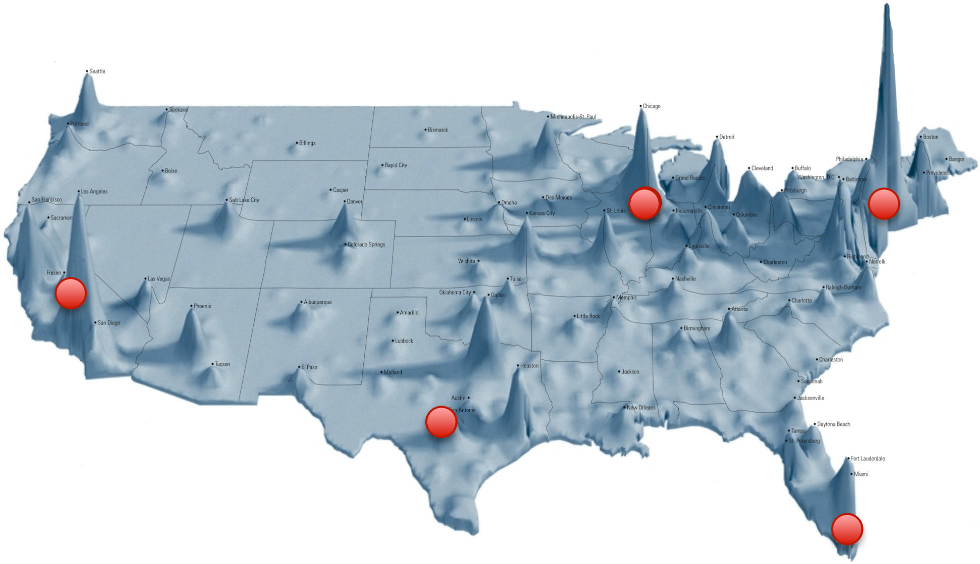
- Strategy:
  - Mark random bills and follow them as they are used
  - Sample full system based on transaction frequency and amount



Simulation method following Metropolis procedure

Parallel Problem: Measuring capital flow

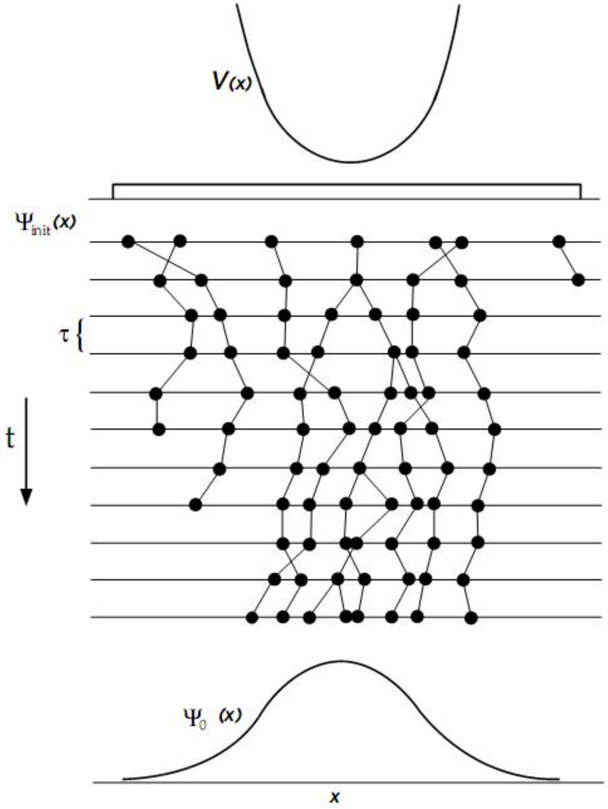
- Strategy:
  - Mark random bills and follow them as they are used
  - Strength – No problems with singular effects, no model dependency, parallelizes well
  - Weakness – May require many samples (marked bills) to accurately represent economy



Simulation method following Metropolis procedure

Quantum Monte Carlo uses statistical sampling to solve the Schrödinger equation

- Electron configurations are sampled randomly via many body Green's Function
  - Natural parallelism over walkers
- Wavefunction we would like to sample from is not positive everywhere (Pauli exclusion principle applies)
- Assume we know where wavefunction changes sign and force walkers to never cross this boundary
  - Fermion sign problem
  - Most fundamental research question in QMC



J. Needs, M. D. Towler, N. D. Drummond, and P. Lopez-Rios,
Casino Version 2.2 User Manual, University of Cambridge , Cambridge (2008)

The accuracy of DMC has been exploited for several decades

- In 1980 Ceperley and Alder used DMC to calculate the energy of the electron gas
- Results underpinned the basis for many generations of DFT exchange correlation functionals
- Used exponentially scaling version of DMC (released node)
- Took advantage of symmetry

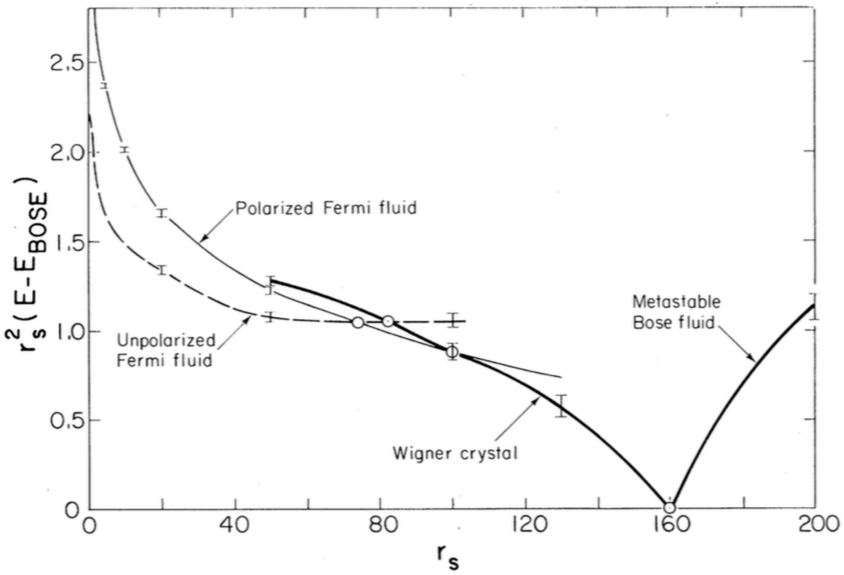
Ground State of the Electron Gas by a Stochastic Method

D. M. Ceperley
National Resource for Computation in Chemistry, Lawrence Berkeley Laboratory, Berkeley, California 94720

and

B. J. Alder
Lawrence Livermore Laboratory, University of California, Livermore, California 94550
(Received 16 April 1980)

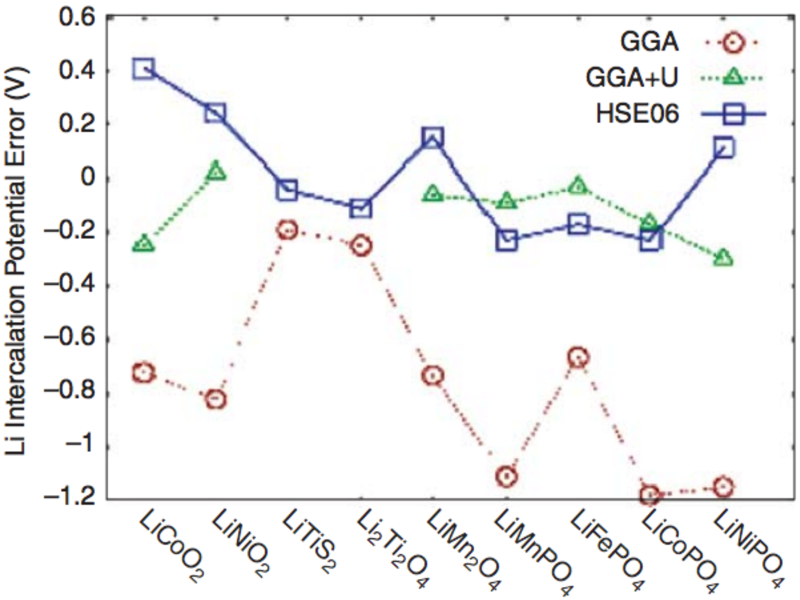
An exact stochastic simulation of the Schroedinger equation for charged bosons and fermions has been used to calculate the correlation energies, to locate the transitions to their respective crystal phases at zero temperature within 10%, and to establish the stability at intermediate densities of a ferromagnetic fluid of electrons.



Why apply this to real materials?

There is a clear need for more accurate methodologies compared to standard approaches even for "successful" cases

Metal Oxides



Ceder MRS Bull 35 693 (2010)

Interstitial defects in Aluminum

Formation Energy (eV)

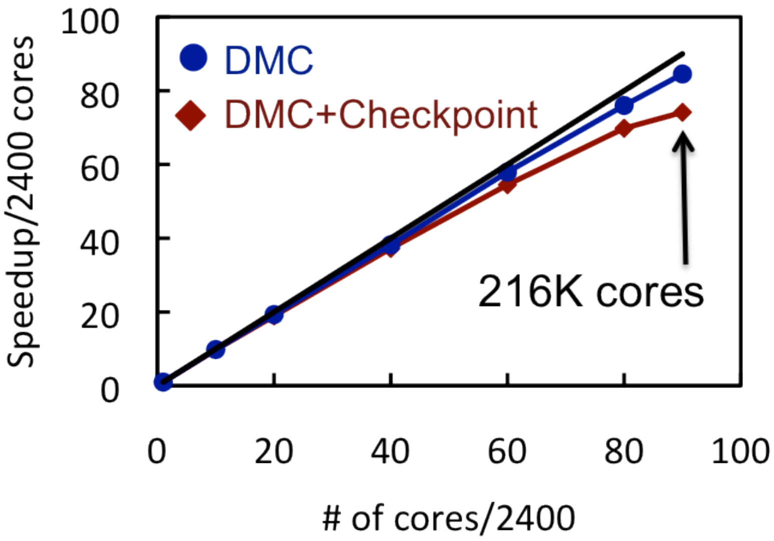
Interstitial	PBE DFT	DMC	Expt
<100>-dumbbell	2.70	2.94	3.0, 3.2(5)
octahedral	2.91	3.13	-
tetrahedral	3.23	3.56	-

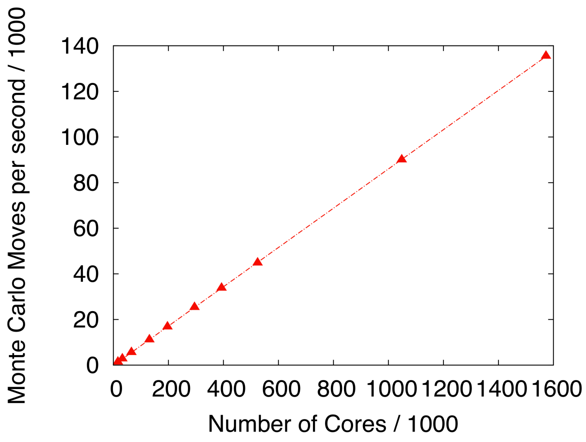
Hood et al. PRB 85 134109 (2012)

Experimental data for many quantities and materials of interest is sparse e.g. surface energies, defect energies.

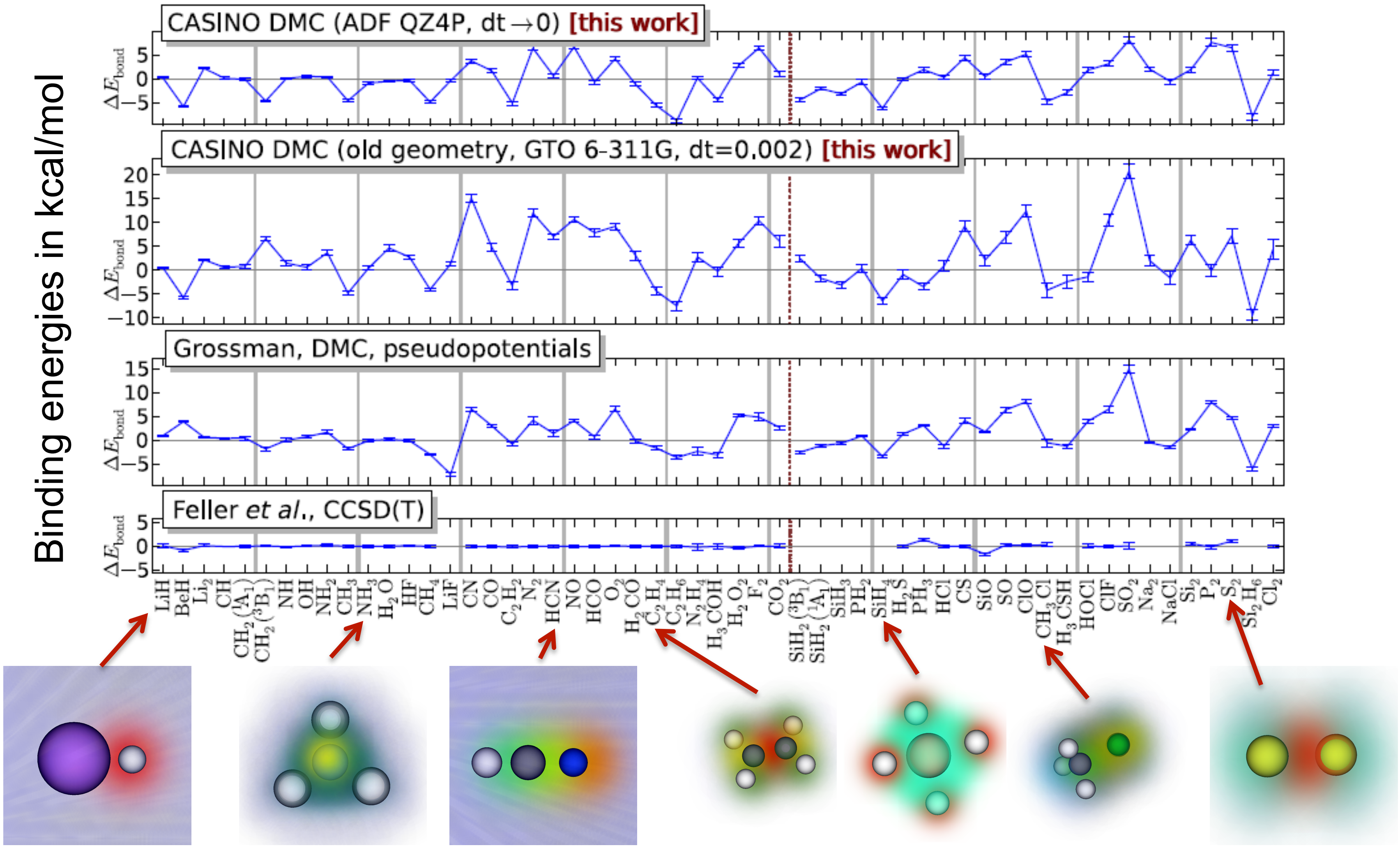
QMCPACK – Massively Parallel QMC

- Quantum Monte Carlo code designed for massive parallelism
- Developed by J. Kim et al at Oak Ridge National Laboratory
- Hybrid MPI / OpenMP parallelism
  - Shared Memory on Nodes, Distributed between
- Can efficiently scale to more than 1,000,000 CPU cores
- CUDA port to GPUs with 15X speedup


Scaling on Jaguar_pf


Scaling on Sequoia

DMC may allow required accuracy



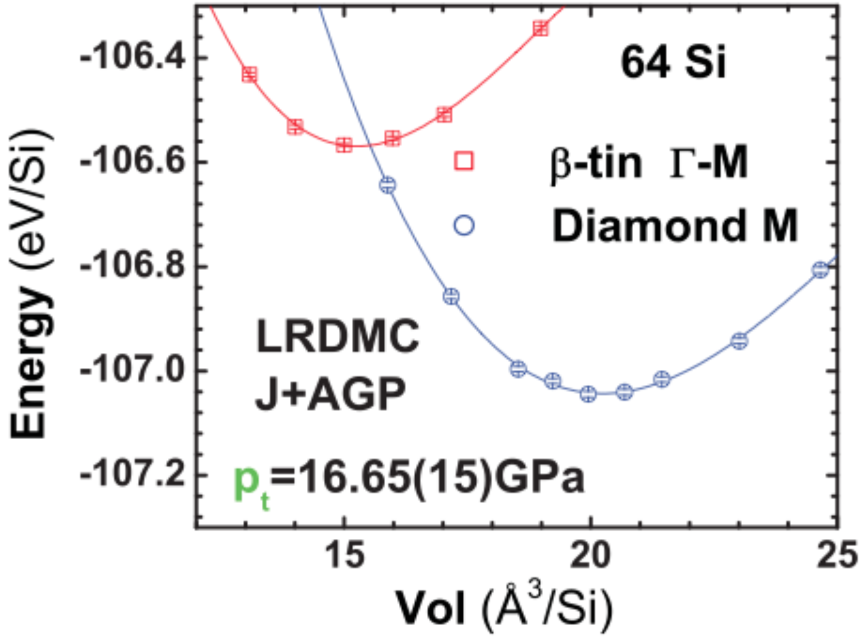
- from Nemec et al, JCP. **132**, 034111 (2010)

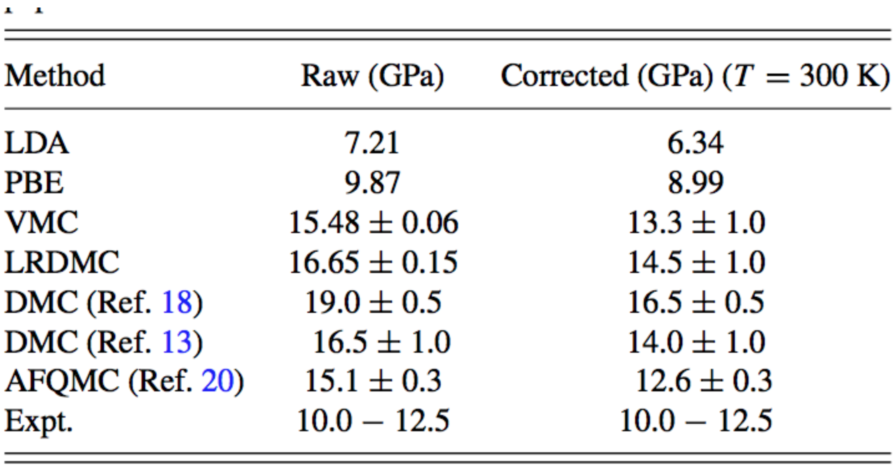
DMC is not as mature as DFT

- Calculations of condensed phases involve a variety of approximations
  - Most approximations may be made arbitrarily small, but approaches to this are not standardized
- Finite size effects
  - One body effects -> DFT comparison or **twist averaging**
  - Two body effects -> Extrapolation, KZK functional or **MPC / Chiesa combination**
- Fixed node errors
  - **Slater jastrow wavefunction**, self healing, backflow, geminals, pfaffians, multideterminants
- Pseudopotentials
  - Only valence electrons simulated because of computational cost
  - In which approximation should core and valence be separated
  - Correction via all electron calculation or comparison with all electron DFT

Approximation methods can greatly affect results

- Case study on Si
- Total energies of diamond and beta-Sn phases calculated with DMC / LRDMC
- Quasiharmonic phonon corrections included



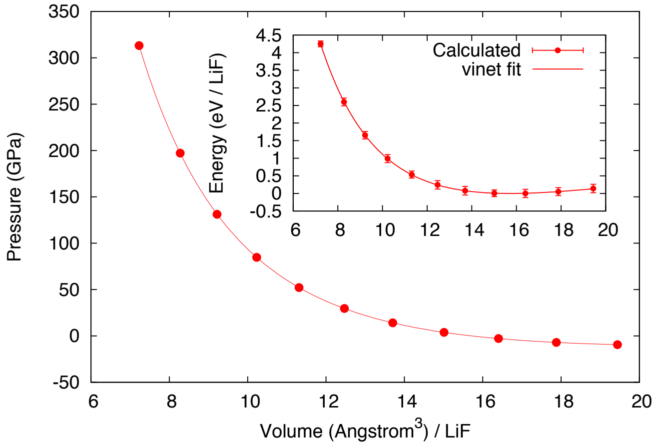


Method	Raw (GPa)	Corrected (GPa) ($T = 300$ K)
LDA	7.21	6.34
PBE	9.87	8.99
VMC	15.48 ± 0.06	13.3 ± 1.0
LRDMC	16.65 ± 0.15	14.5 ± 1.0
DMC (Ref. 18)	19.0 ± 0.5	16.5 ± 0.5
DMC (Ref. 13)	16.5 ± 1.0	14.0 ± 1.0
AFQMC (Ref. 20)	15.1 ± 0.3	12.6 ± 0.3
Expt.	10.0 – 12.5	10.0 – 12.5

Sorella et al. PRB 83, 075119 (2011)

Test approximations on a suite of solids

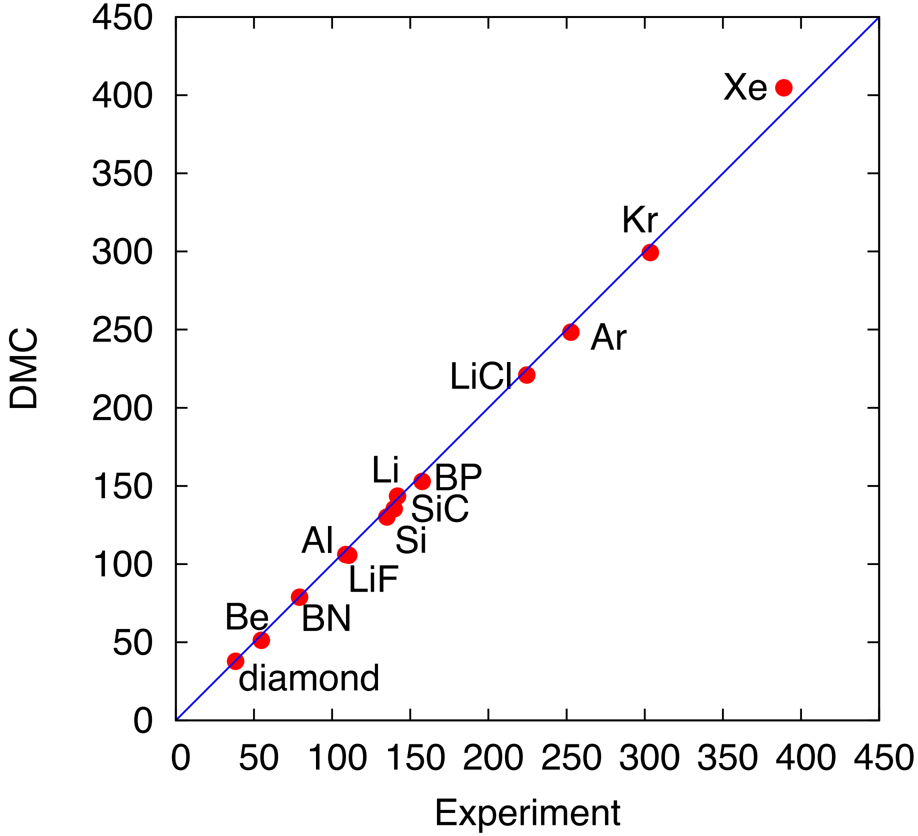
- Binding is different
  - Far less effect from degenerate energy levels at highest energy states
  - More effect from relative energy levels
- Test should compare to easily measured experimental data
  - high pressure calculations to derive properties of ambient phase
- Previous calculations have required 1 year of time on NSF machines for a single solid
- Calculations performed on Cielo



First ever extensive benchmarks of Quantum Monte Carlo for condensed matter

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

Equilibrium Volume (bohr^3)

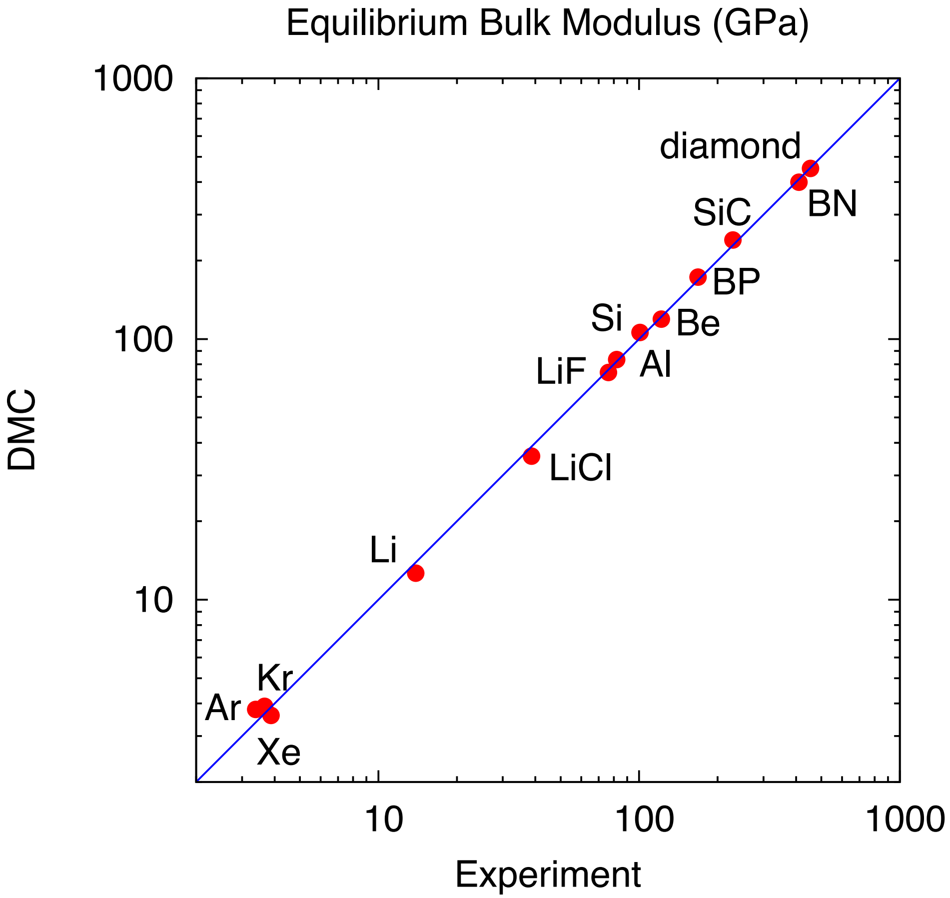


- Materials span a factor of 10 in equilibrium volume
- Four types of bonding are included
  - Ionic
  - Covalent
  - Metallic
  - Van der Waals
- Lattice Constants within ~0.9%
- This provides a new baseline procedure for a QMC calculations

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%

First ever extensive benchmarks of Quantum Monte Carlo for condensed matter

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

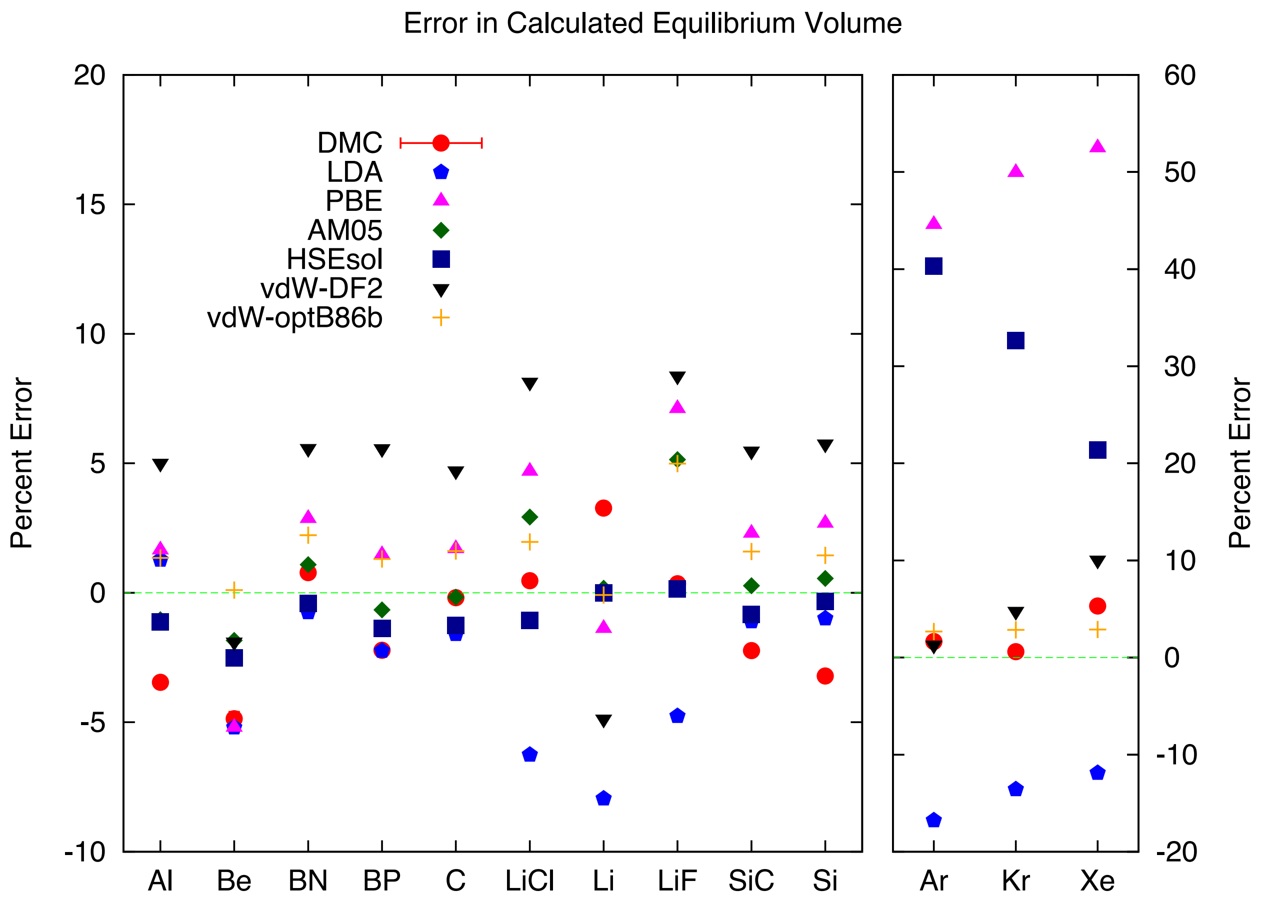


- Bulk modulus spans over 3 orders of magnitude
- This provides a new baseline procedure for a QMC calculations

Mean error: -0.07 +/- 0.42
Mean absolute error: 3.53 +/- 0.42
RMS error: 0.62 +/- 0.44%
Mean absolute relative error: 4.49 +/- 0.44%

Compare to DFT functionals

- **Compare to various "good" DFT functionals**
  - **LDA**
  - **PBE**
  - **AM05**
  - **HSEsol**
  - **vdW-DF2**
  - **vdW-optB86b**
- **Non van der Waals functionals yield high quality results on many materials**
  - **But not noble gases**
- **van der Waals functionals are improving to wide applicability**



LNS and TRM, PRB 88, 245117 (2013)

Compare to DFT functionals

- **Compare to various "good" DFT functionals**
  - LDA
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  - AM05
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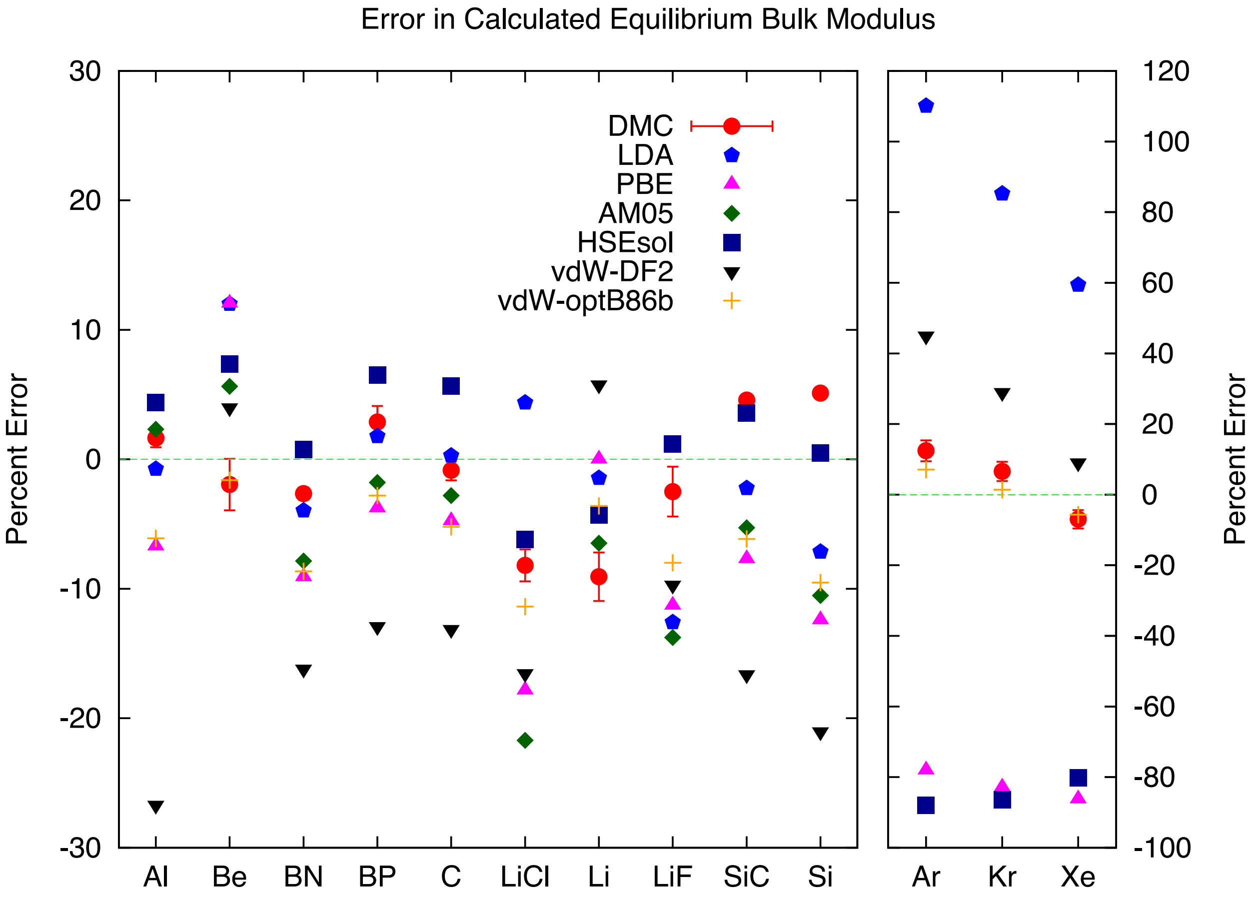
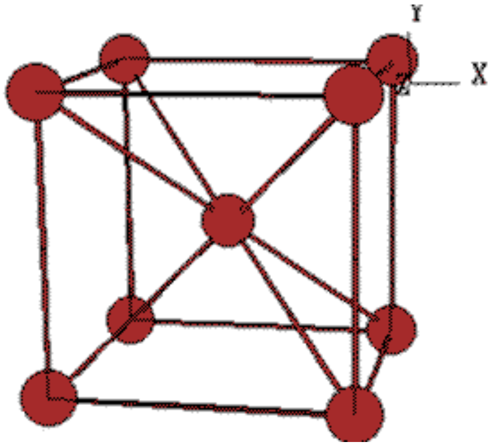


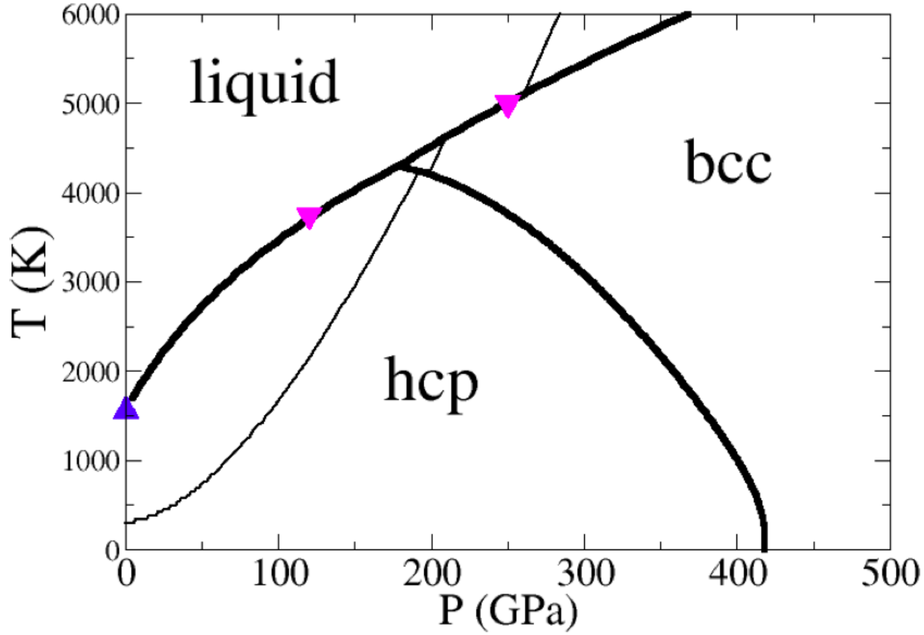
LNS and TRM, PRB 88, 245117 (2013)

Study simpler system to isolate errors:

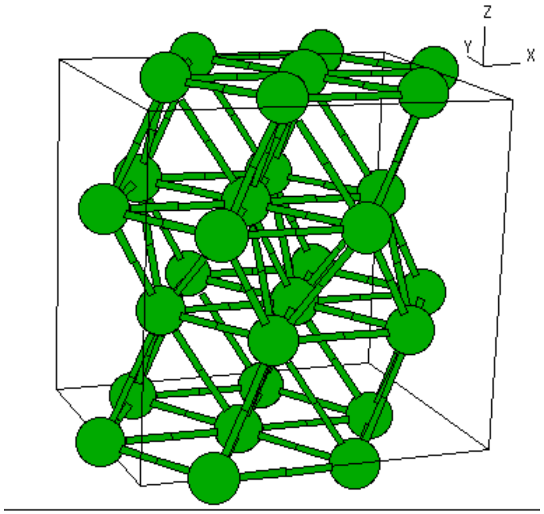
Be HCP -> BCC phase transition

- Solid Be used in ICF
  - High strength, low Z material, Low x-ray absorption
- HCP at ambient temperature and pressure
- Phase transition to BCC at high pressure
- Simple but demanding computationally





Benedict et al. PRB **79**, 064106 (2009)



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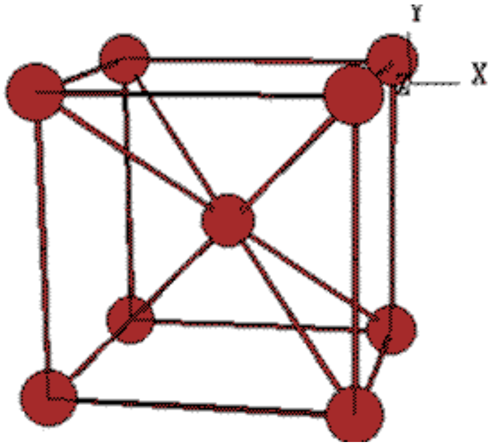
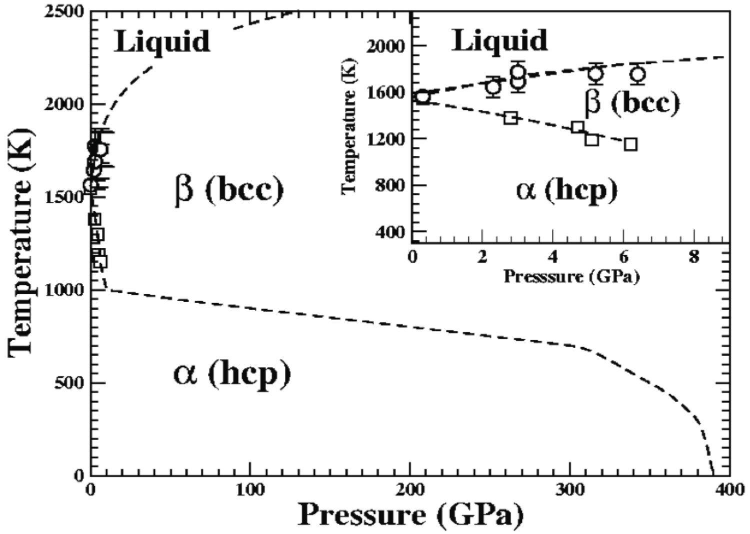
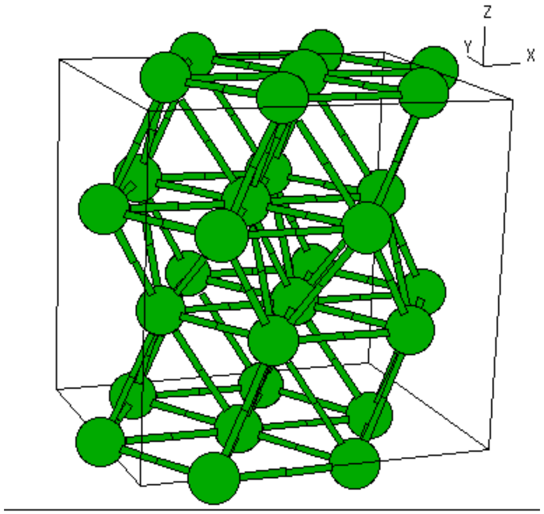


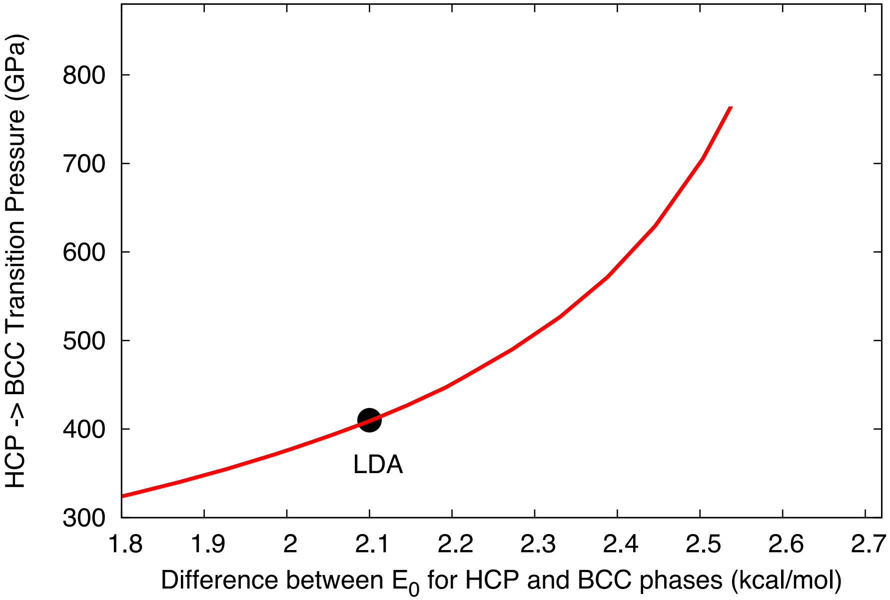




Rober and Sollier. J. Phys. IV France **134**, 257 (2006)

Extreme sensitivity to errors

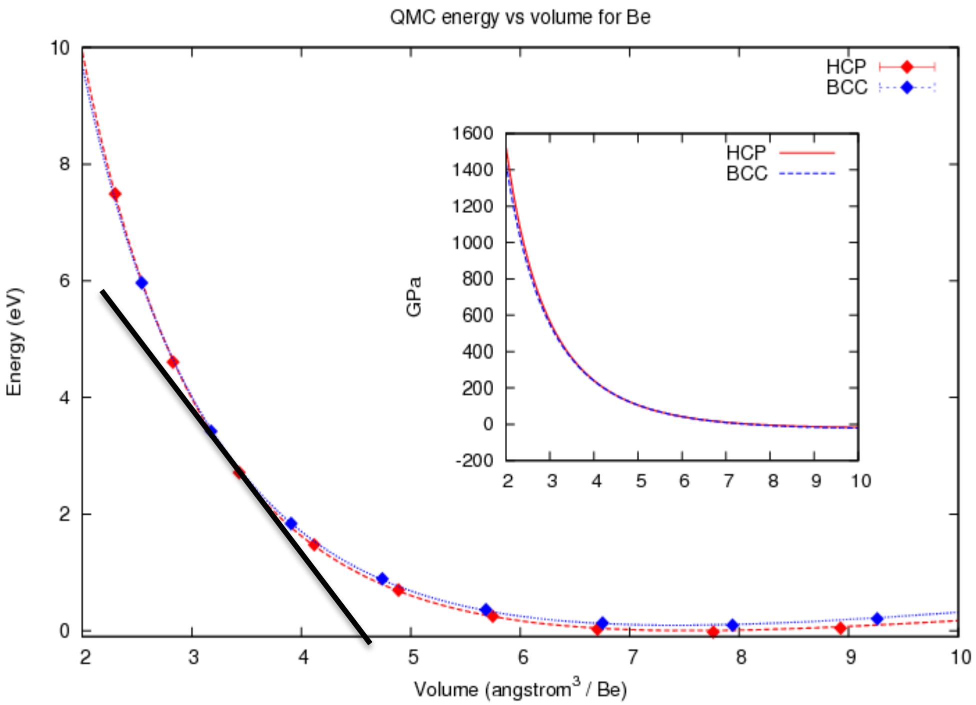
- Calculate beryllium HCP-> BCC phase transition pressure with LDA+QHA
- What is sensitivity of transition?
  - Make constant shift of $E_{BCC}(V)$
    - Transition pressure changes from ~400 GPa to 550 GPa with a 0.3 kcal/mol shift
- “Chemical Accuracy” is not good enough!



Study simpler system to isolate errors:

Be HCP -> BCC phase transition

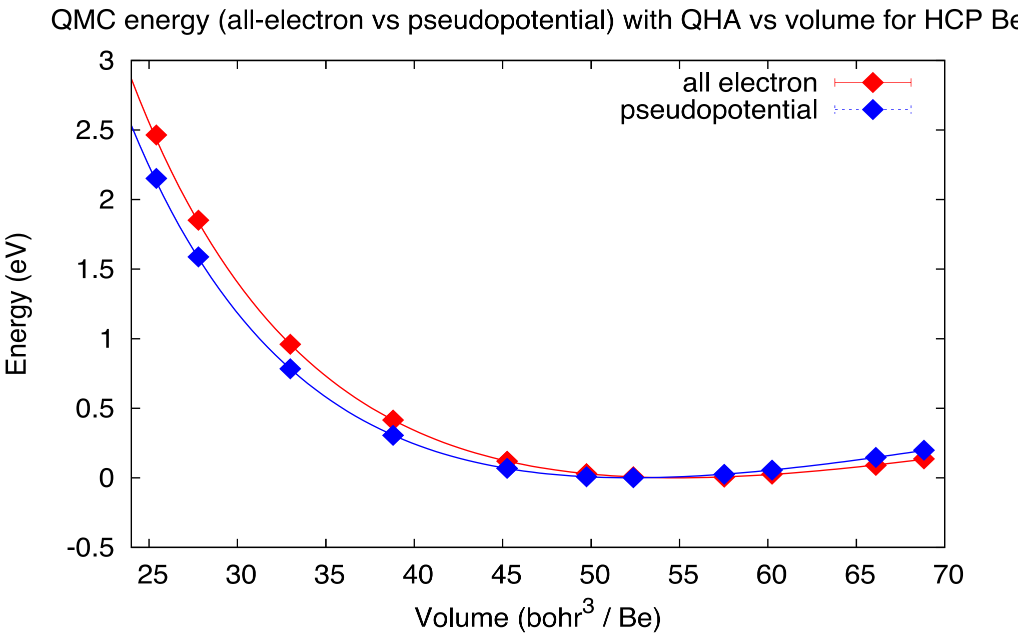
- **Equation of state is fit using Vinet form**
  - More crucial because values have statistical errors
- **Casula t-move formalism employed for pseudopotentials**
- **Phase transition occurs at > 635 GPa**
  - Significantly higher than DFT result ~ 410 GPa



HCP Equilibrium Parameters

	QMC	Exp
c/a	1.569 +/- 0.004	1.568
V_0 (angstrom^3)	7.746 +/- 0.078	8.117
Bulk Modulus (GPa)	124 +/- 2	116.8

Perform all electron calculation to eliminate pseudopotential errors



- **Utilize hard pseudopotential with 4 electrons in valence for calculation of trial wavefunction**
- **Replace with 4/r for QMC**
- **All properties of HCP (ambient) phase agree with experiment**
- **Phase transition pressure shifts to 418 GPa, more in line with that inferred by shock experiments**

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	8.123 +/- 0.006	8.117
Bulk Modulus (GPa)	124 +/- 2	115.7 +/- 1.5	116.8

BFD Hartree-Fock based pseudopotentials improve agreement but have limitations

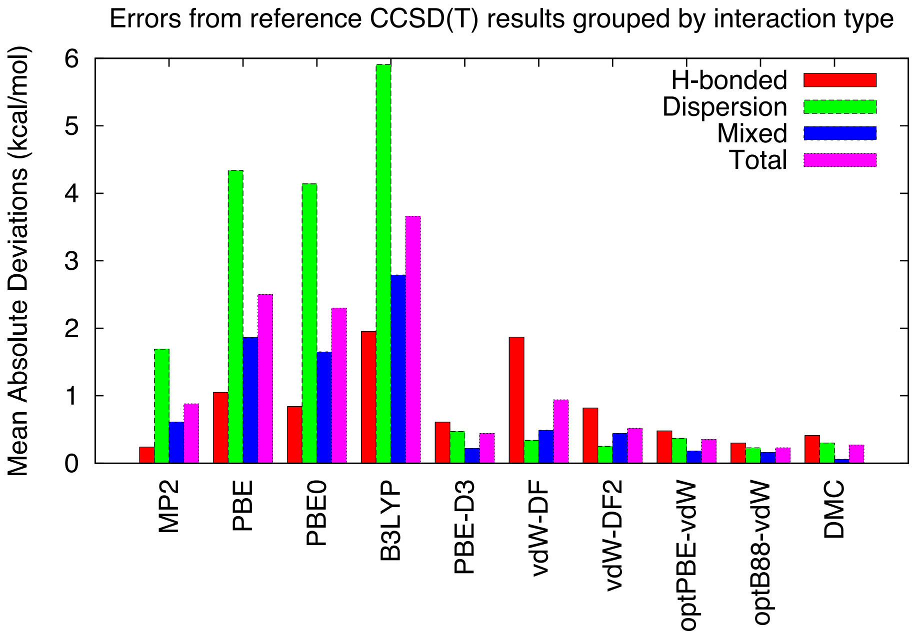
- Hatree-Fock based PPs have previously been shown to perform better in quantum chemical calculations
- BFD HF pseudopotentials improve agreement with all electron results, suggesting a path for improving pseudopotential development

HCP Equilibrium Parameters

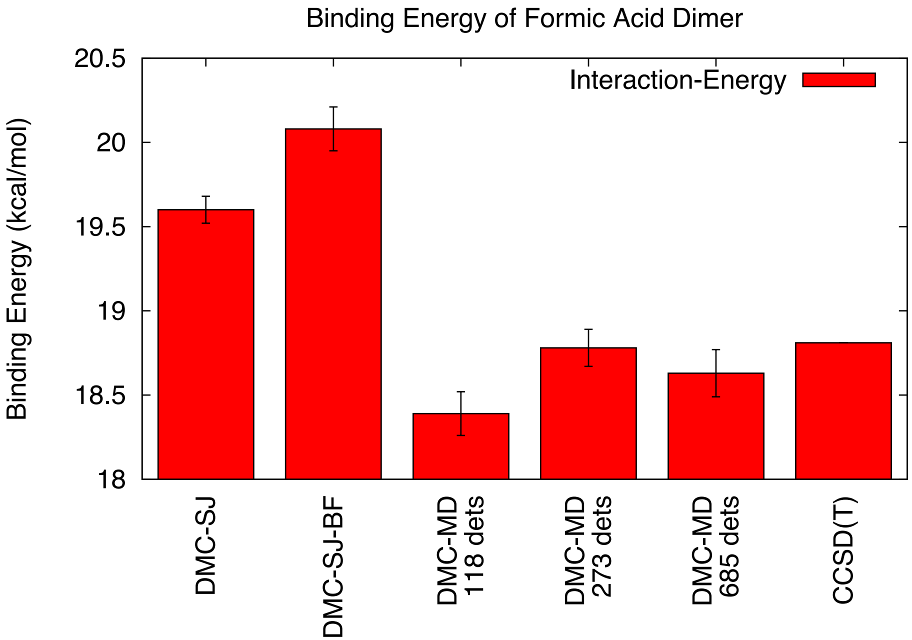
	LDA PP QMC	BFD PP QMC	All Electron QMC	Exp
V_0 (bohr^3)	52.27 +/- 0.02	55.19 +/- 0.01	54.87 +/- 0.03	54.776
Bulk Modulus (Gpa)	124.21 +/- 0.74	112.99 +/- 0.43	115.69 +/- 1.04	116.8

Systematic test of DMC for dispersion in chemistry (S22 test set)

- The S22 test set collects complexes of molecules bound by dispersion
  - Hydrogen bonded complexes
  - Dispersion bonded complexes
  - Mixed binding complexes
- DMC with a single slater jastrow trial wavefunction is applied
- Performance compared to CCSD(T) is equal to or better than competing methods



DMC can be systematically improved for chemical systems

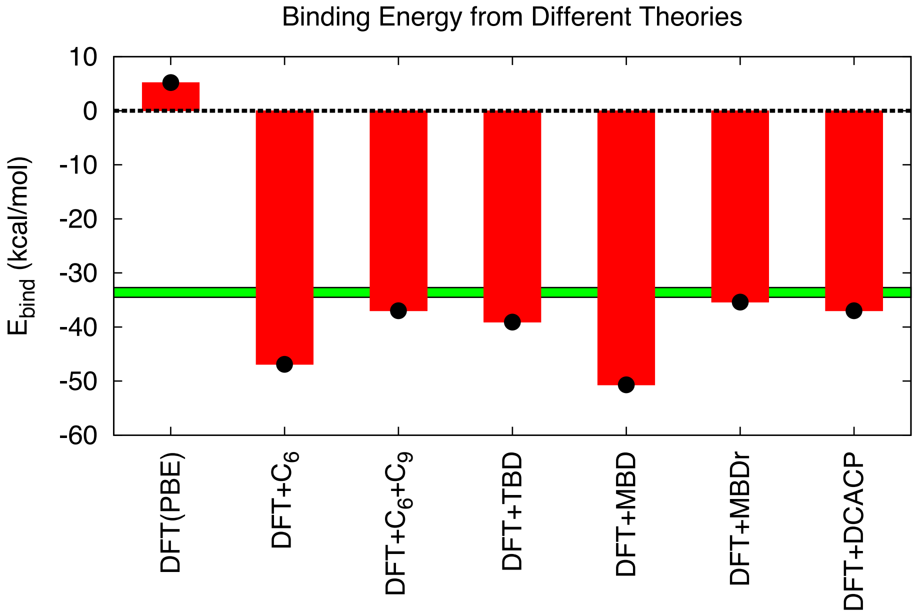


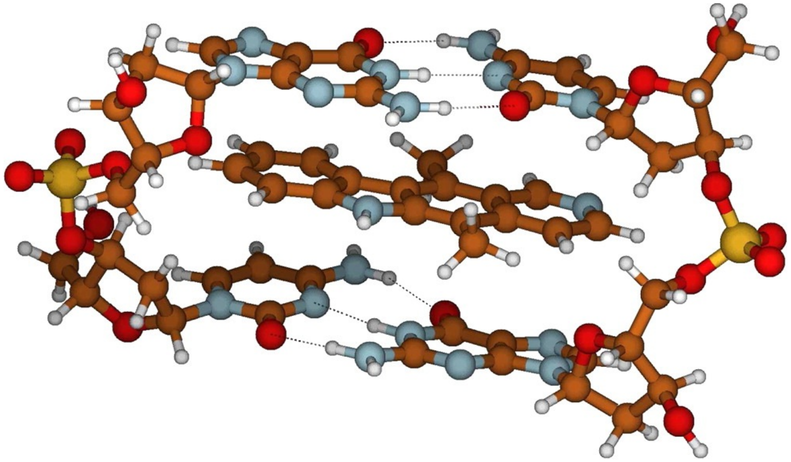
- The formic acid dimer had the largest error using single slater-jastrow wavefunction
- Adding a backflow transformation does not uniformly improve fragments and complex
- Increasingly large multi-determinant expansions chosen by CISD calculations systematically reduce residual error

BEYOND BENCHMARKS

DMC can be used to benchmark other methods when applied to large chemical systems

- There is an emerging consensus that high accuracy is already obtained for van der Waals interactions using current techniques & approximations.
- Large systems are accessible with cubic scaling QMC today. Here, used to validate different van der Waals approaches.



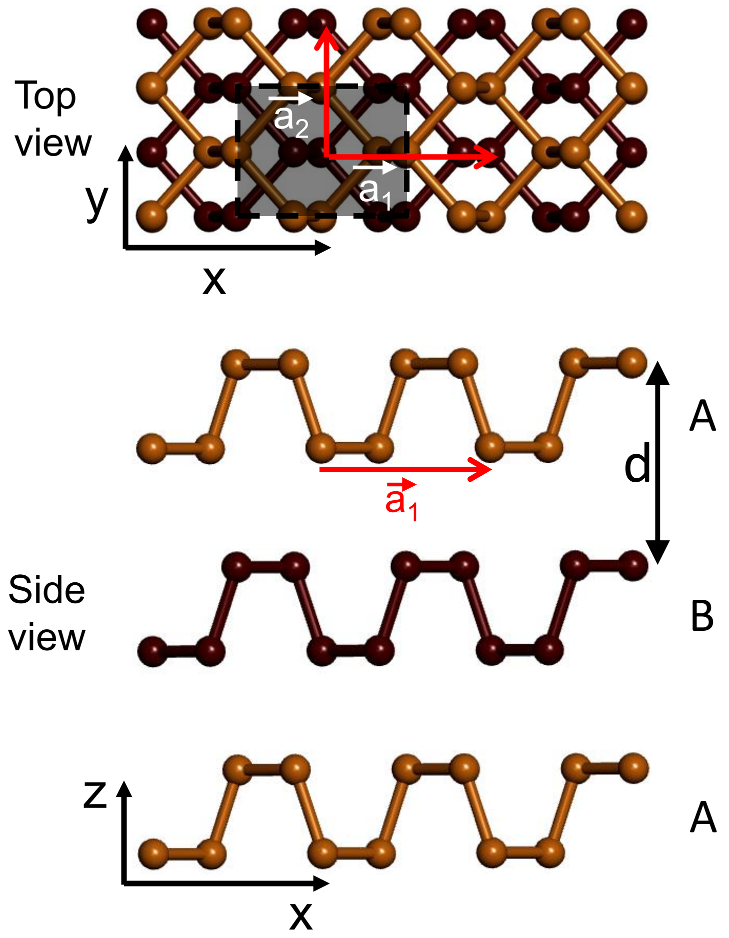


DFT+MBDr method closest to DMC for Ellipticine-DNA binding.
Collaboration with Anatole von Lilienfeld (ANL, now Basel)

Benali JCTC **10** 3417 (2014)

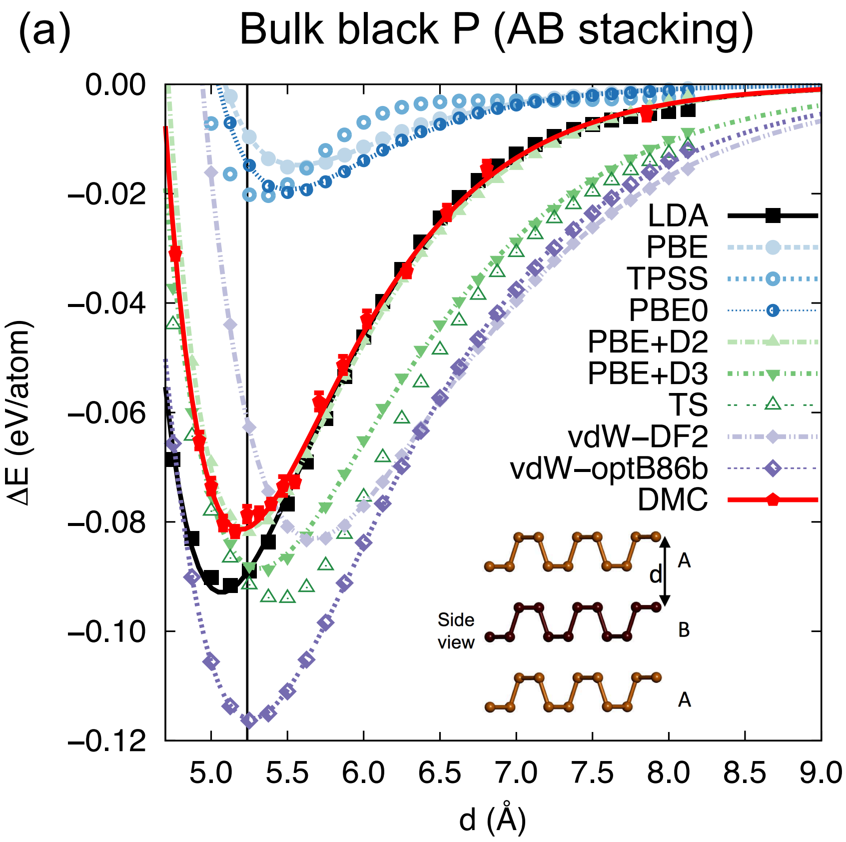
Black phosphorus: a promising new layered material

Bulk black P
(AB stacking)



- 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

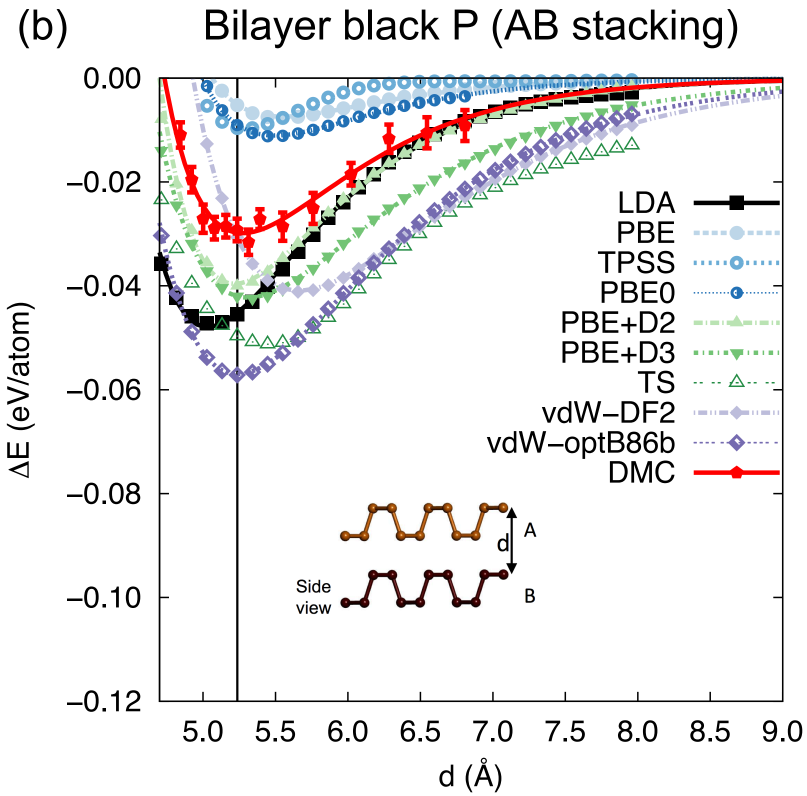
Calculations on bulk black phosphorus yield good structure compared to experiment



- Excellent agreement for interlayer separation between DMC and experiment
- DFT+D2 also shows excellent performance for both binding energy and geometry
- Treatment of exchange does not seem to be significant on its own – see sequence PBE, TPSS, PBE0
- Van Der Waals corrected functionals have widely varying predictions

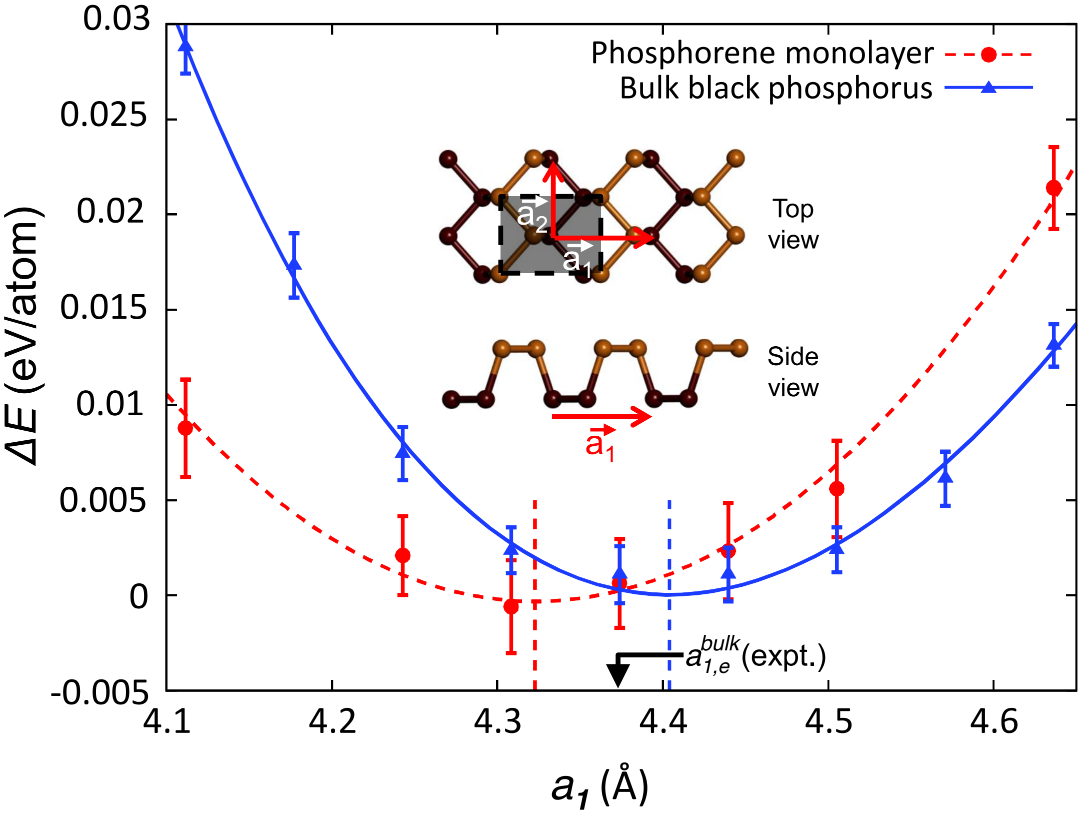
Varying the stacking of the a bilayer suggests steric effect

- 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



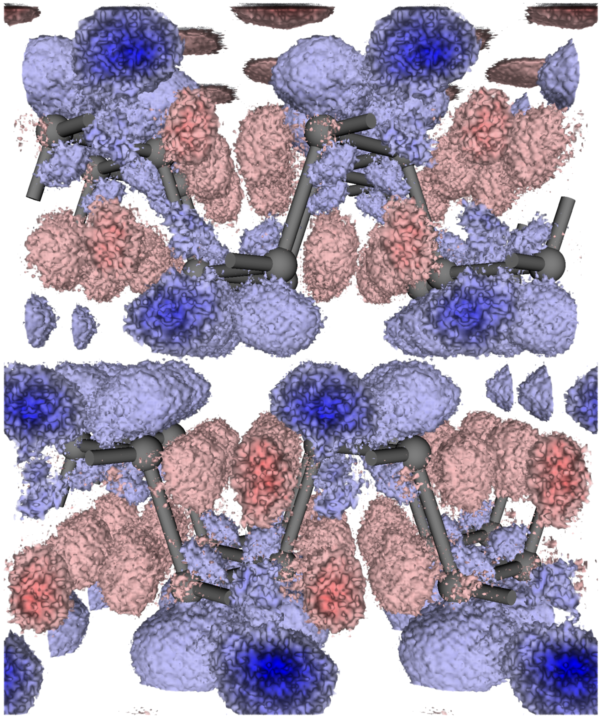
Intralayer geometry is sensitive to environment

- 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

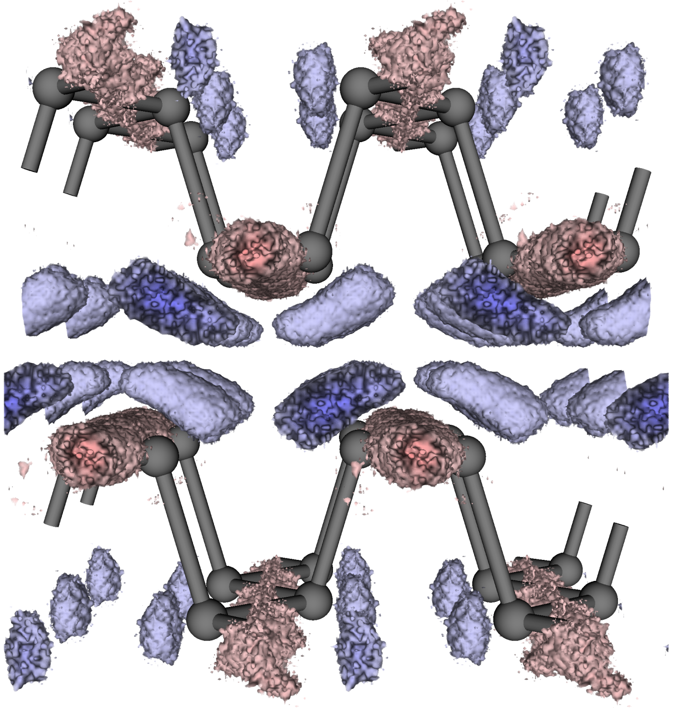


Phosphorene exhibits large charge redistribution due to the effects of the environment

Bulk charge density difference



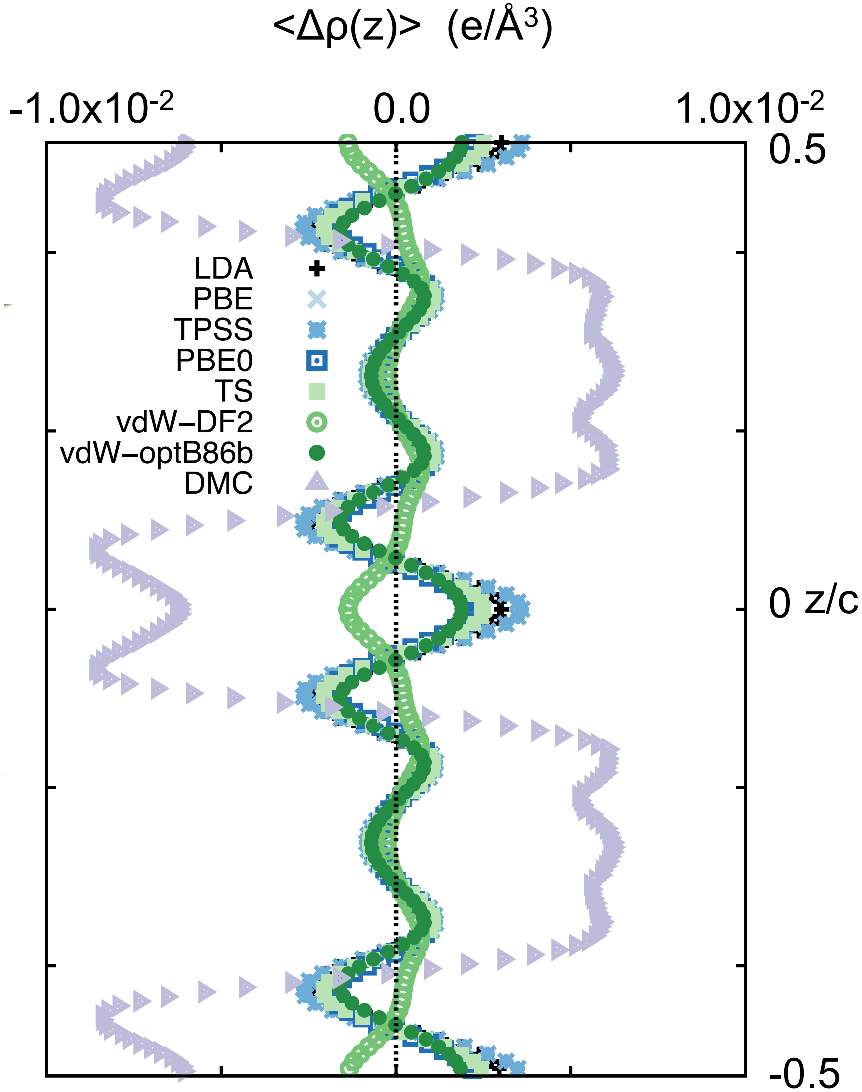
Bulk charge density difference



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

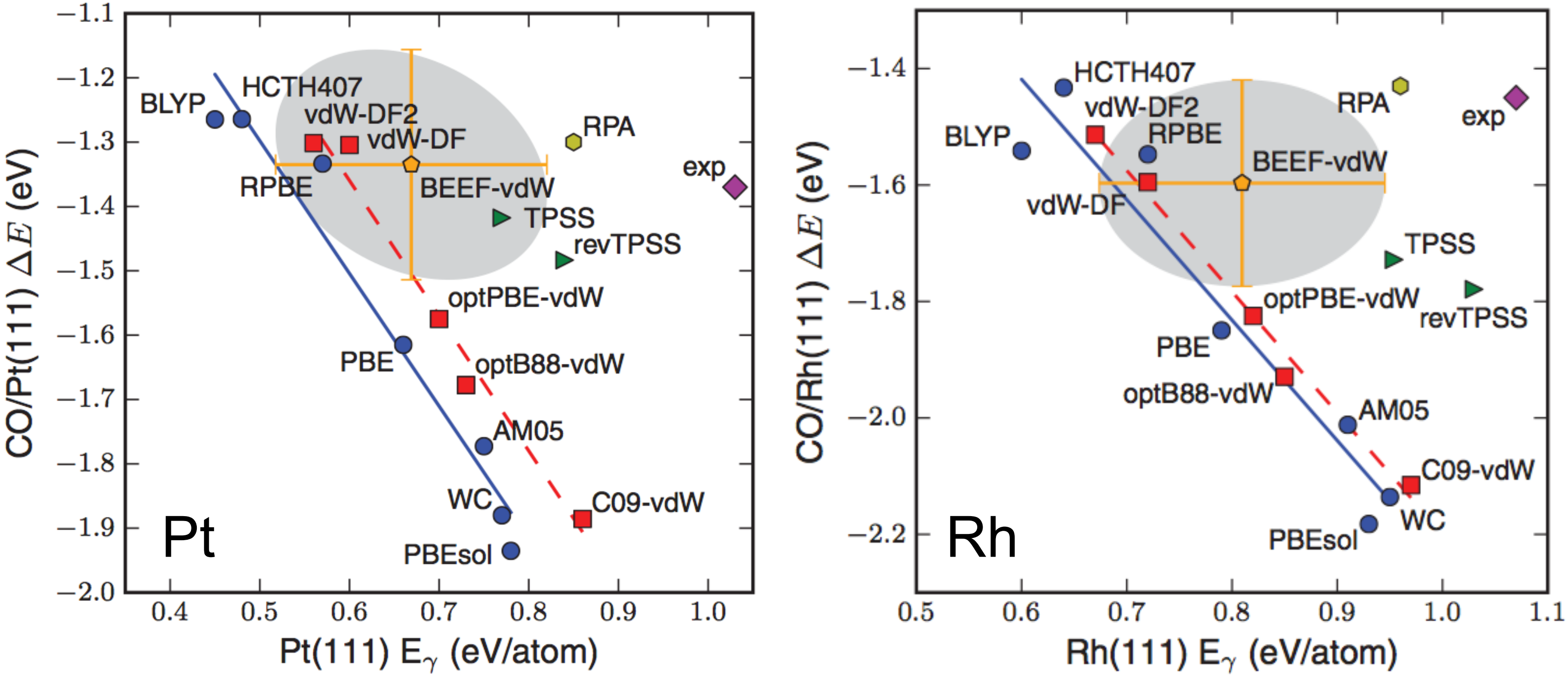
This charge redistribution presents a challenge for DFT functional development

- Van der Waals functionals generally do not predict qualitatively right behavior of charge density to interactions
- Charge density is the central quantity around which DFT is built
- If the charge density is incorrect, can other calculated properties be relied upon?



QMC for catalytic surfaces and catalysis

- Accurate adsorption and reaction barrier energies for typical catalytic species remain a grand challenge.
- The variation between different electronic structure predictions is physically consequential. This limits catalysis design & optimization.
- Feibelman famously observed the CO adsorption problem on Pt for DFTs

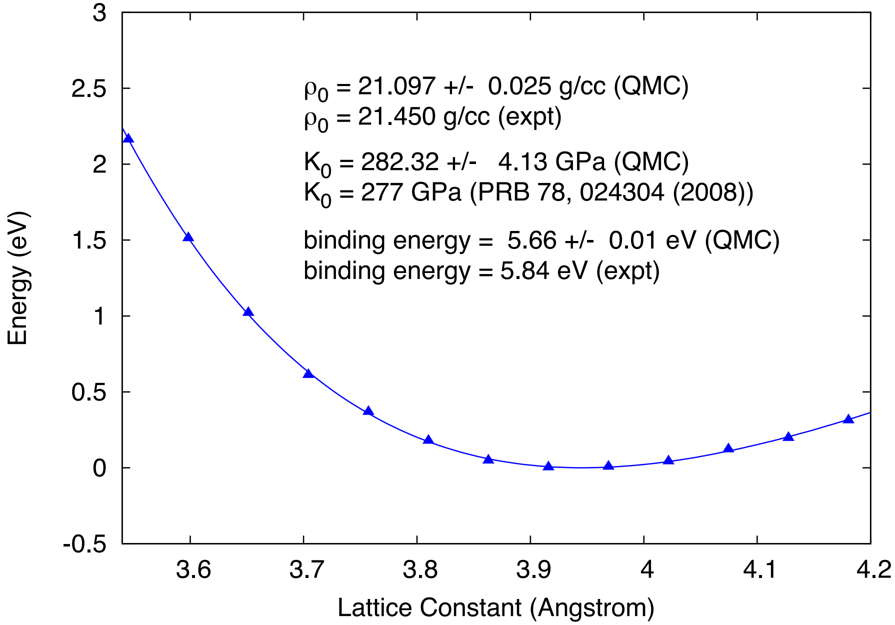


Wellendorff PRB 85 245149 (2012) RPA: Schimka Nat. Mat 9 741 (2010)

No functional or information theoretic combination of functionals reproduces the experimental surface energy and CO adsorption energy for Pt or Rh.

Revise pseudopotential generation scheme and apply to heavier elements

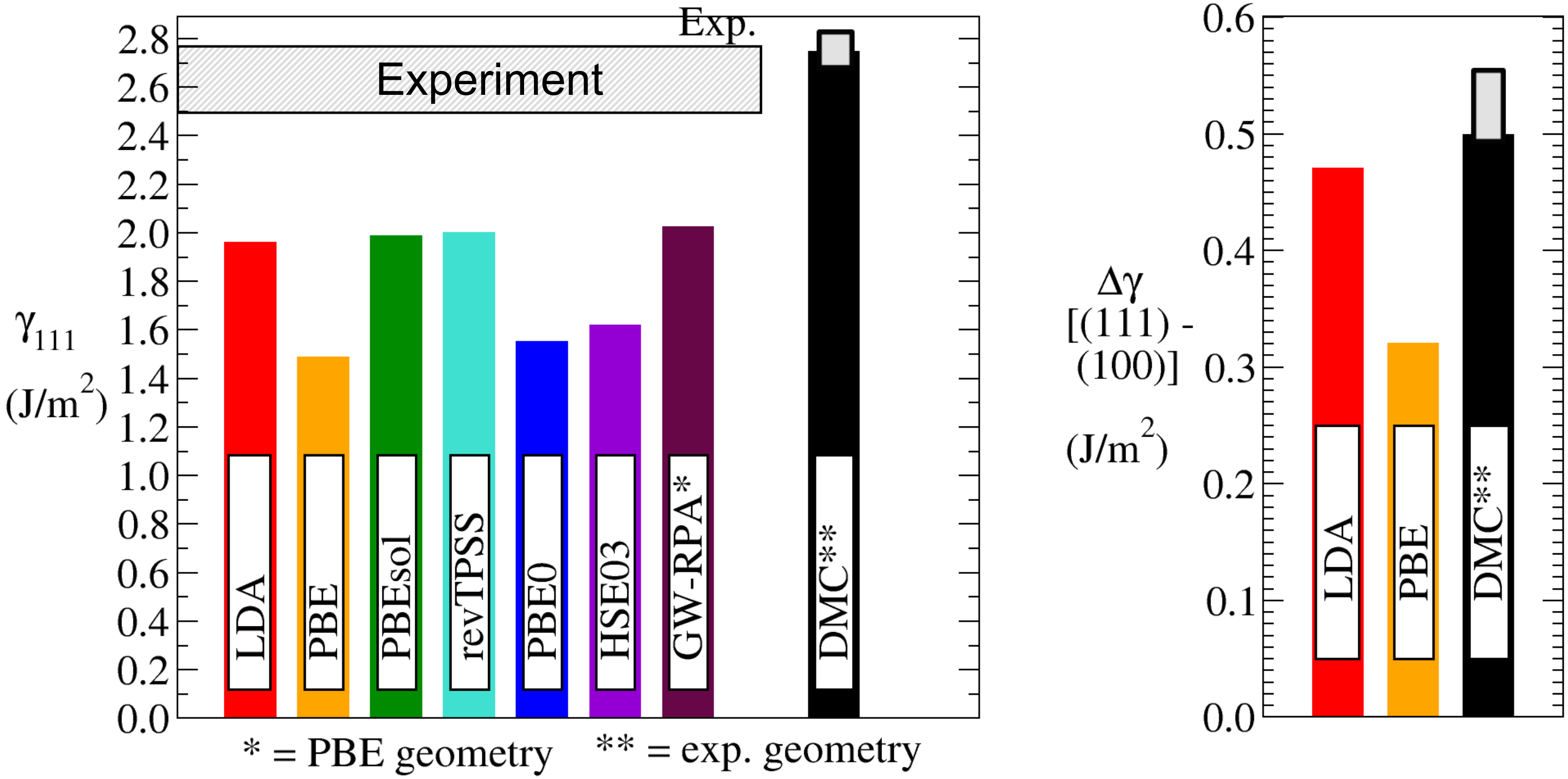
- Still require DFT based pseudopotentials to accurately reproduce all electron results
- Attempt to reduce size of locality error by making nonlocal channels similar to local
- Preserve Kleinman-Bylander form for DFT, but allow change of local channel for DMC
- Choose core-valence separation based on separation in energy



Application to FCC platinum yields encouraging results for ambient density, bulk modulus and cohesive energy

QMC for catalytic surfaces and catalysis

- We have computed the Pt (111), Pt (100) surface energies. Aim to confirm and explain difference w.r.t. DFTs, then compute adsorption energies and other surfaces. Initial study includes outermost surface relaxation.
- Paper on Pt clusters submitted to JCTC (2015).
- Experimental surface energy data is limited!

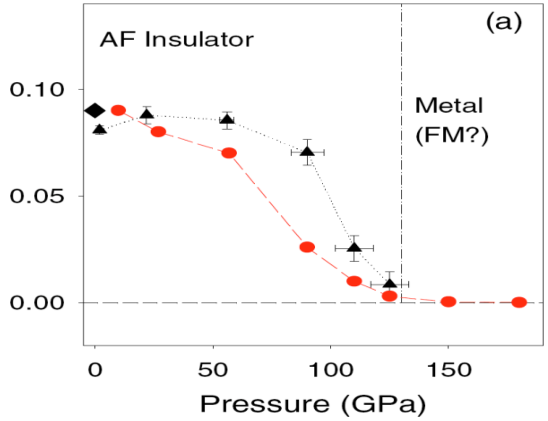


Unpublished, ongoing work. DFT data: L. Schimka et al. Nature Materials **9** 741 (2010), J. Sun et al. PRB **83** 121410 (2011)

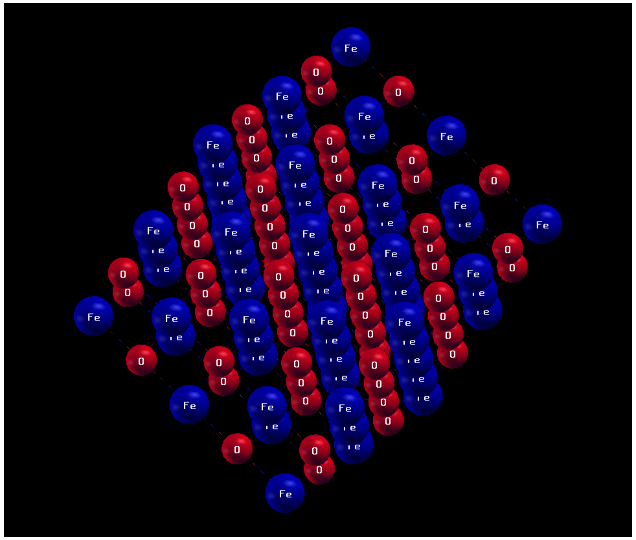
Improving fidelity for systems with strongly correlated electrons: FeO magnetic states

Sandia National Laboratories

- **At ambient pressure FeO is an antiferromagnetic insulator with a rock salt structure**
- **End member of Magnesiowustite (Mg,Fe)O, which is one of most abundant minerals in earth's mantle**
- **Iron 3d states partially filled, but localized**
- **Borderline between a charge transfer and a Mott insulator**
- **Rich electronic structure under pressure with a moment collapse and metallization**



Experimental activation energy for conduction under Pressure from V. V. Struzhkin *et al.*, Mater. Res. Soc. Symp. Proc. **987**, 0987 (2007)

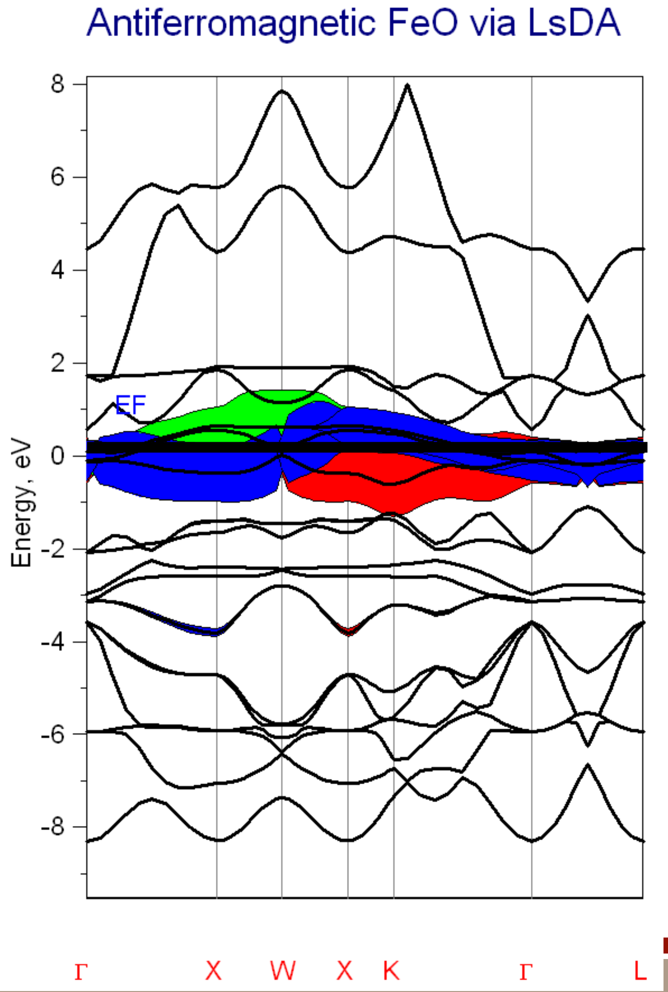


Most DFT functionals qualitatively fail for FeO predicting a metal instead of an insulator

- DFT within the Local Density Approximation
    - Agreement of lattice constant, equilibrium strain, magnetic moment

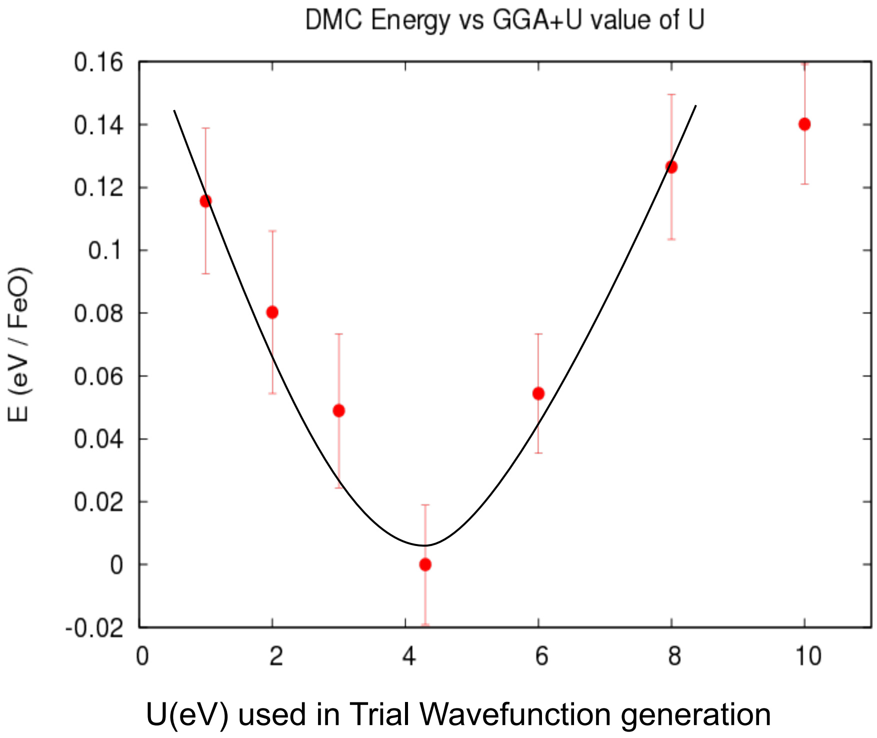
  Cohen, Mazin, and Isaac. Science **275**, 654 (1997)

    - But it is a metal!
- Origin of failure
    - Local functionals do poor job of describing interactions of localized electrons



Evaluating Wavefunctions: Choosing model Hamiltonian with QMC

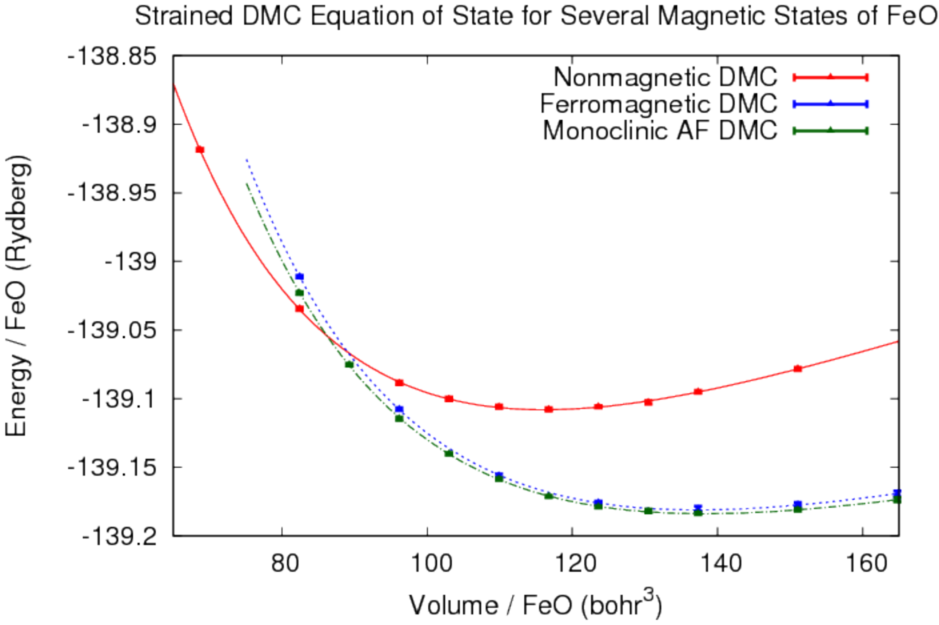
- QMC is variational, so wavefunctions with different Hubbard interaction parameters can be compared on equal footing
- Shallow minimum at U=4.3 eV
- Minimum not strongly dependent on magnetic state or volume
- Does not necessarily confirm LDA+U approach



Predictive results for FeO under pressure: No stable Ferromagnetic State

- FeO undergoes a spin collapse as well as a metal-insulator transition under pressure
- Spin collapse at 178 GPa
- No evidence of Antiferromagnetic to Ferromagnetic transition
- Antiferromagnetic strain increases 0% → 8 %

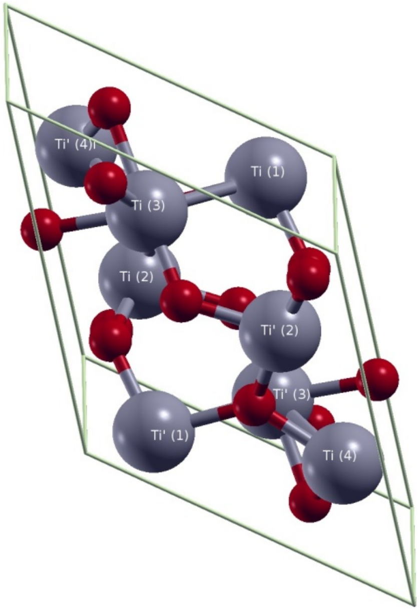
	A_0 (Å)	K_0 (Gpa)	K'_0
Unstrained QMC	4.342(10)	179(11)	4.8(5)
Strained QMC	4.343(8)	165(6)	4.7(3)
Kolorenc QMC	4.324(6)	170(10)	5.3(7)
Experiment	4.334	152.3	4.92



Lattice Const from Hjortsberg et al. PRB **37**, 3196 (1988)
Derivative quantities from McCammon et al., Phys Chem Miner **10**, 106 (1984)
Chart adapted from Kolorenc et al. PRL **101**, 185502 (2008)

Other complicated magnetic structures are accessible: Ti_4O_7 Magnéli phase (Low temperature ~ 120K)

Ti_8O_{14} Unit cells



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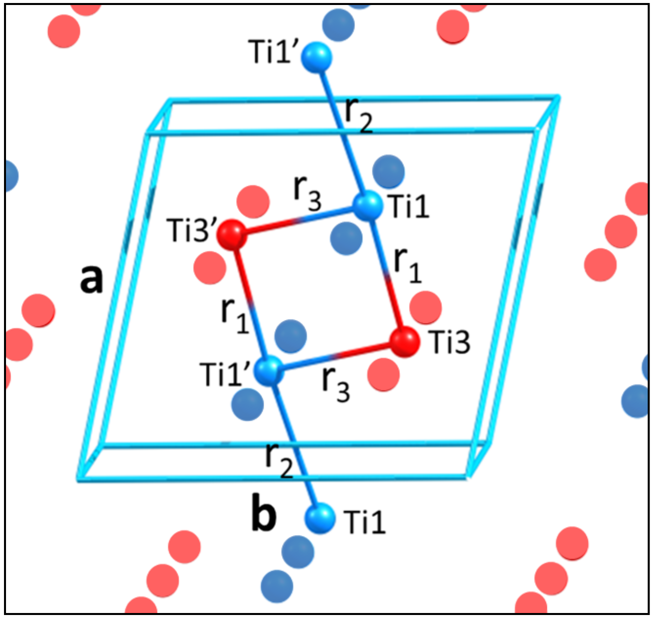
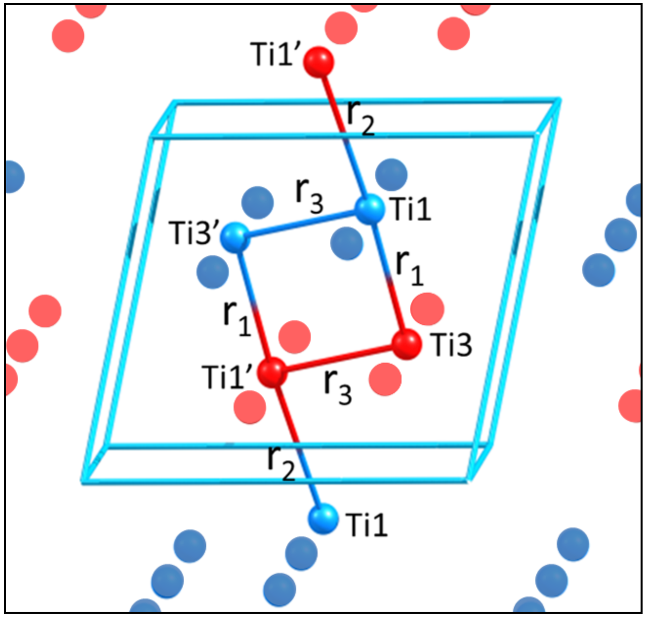


AF1



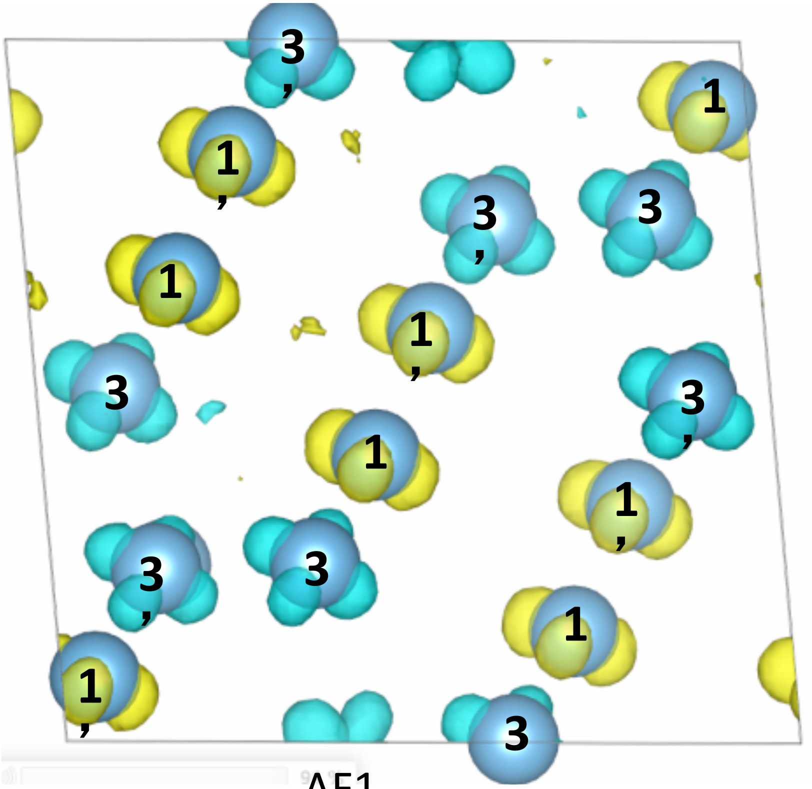
AF3

AF1: (+,0,-,0|+,0,-,0)
AF2: (+,0,+,0|-,0,-,0)
AF3: (+,0,-,0|-,0,+,0)
FM : (+,+,+,+|+,+,+,+)

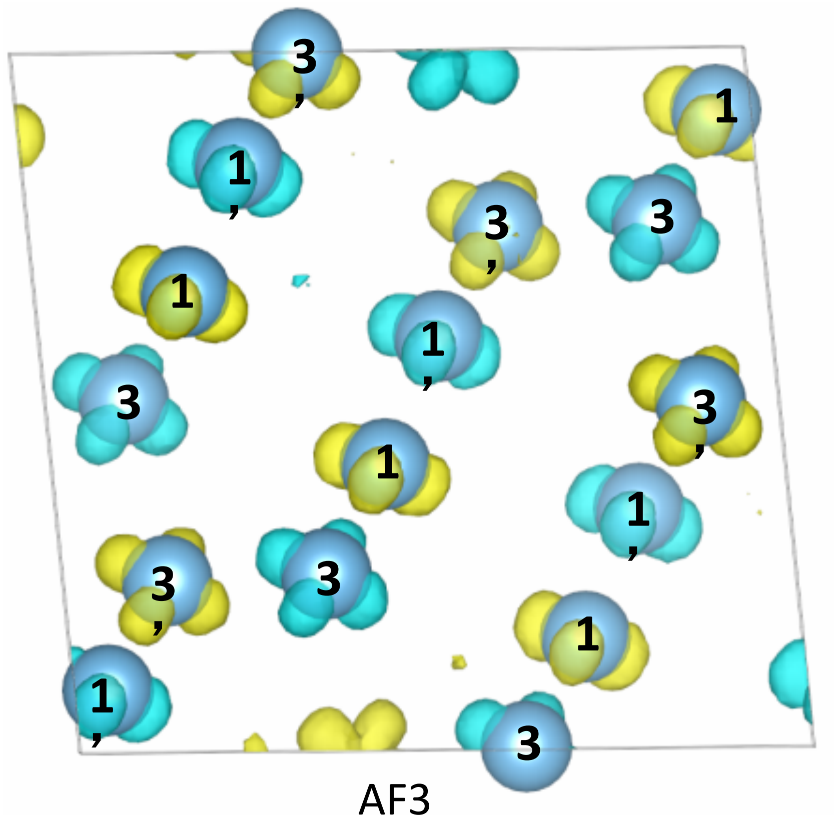
E_{diff} = ~ **4meV/Ti_4O_7** Using LDA +U , LDA +ASIC, HSE06 and All electrons calculations

LDA +U favors the FM state as the ground state while LDA +ASIC and HSE06 favor the AF3 and AF1 over the FM states.

QMC Increases the energy differences between phases in Ti_4O_7

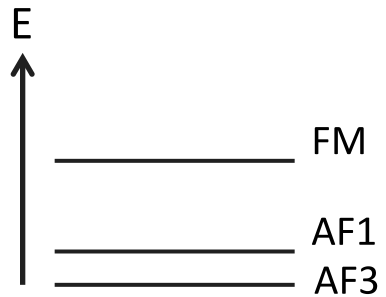


AF1



AF3

	E(FM - AF3) (eV)	E(AF1 – AF3) (eV)
DMC	**+0.1779 ± 0.0134**	**+0.07041 ± 0.01035**
LDA +U	+0.607	+0.004
LDA + ASIC	+0.118	+0.004



DMC has a bright future, but other competitors must be considered

- Quantum chemistry methods provide a rigorous approach to accurate calculations
  - Have only recently been applied to condensed phases
    - See for example: Phys. Rev. Lett. 115, 066402 (2015) and J. Chem. Phys. 143, 102817 (2015)
    - Limitations remain due to scaling of the methods and consequently small basis set sizes
  - New embedding methods promise a wider domain of applicability
    - PRL **109**, 186404 (DMET by Chan group)
    - PRB **89**, 186404 (DET by Scuseria group)
- Biggest challenge appears to remain poor scaling and subsequently small basis sets and active spaces

DMC continues to remain attractive

- Method operates in infinite basis set limit
- Calculations involving hundreds to thousands of electrons are becoming routine
- Dynamical correlation is handled simply and accurately
- Applications to layered materials, van der Waals compounds and transition metal catalysts have yielded high accuracy and point to new physics
- The parallelizability of DMC makes it an ideal fit for leadership class computing facilities