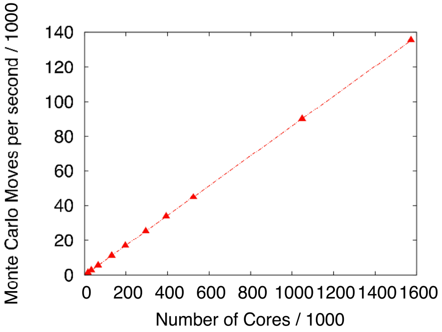
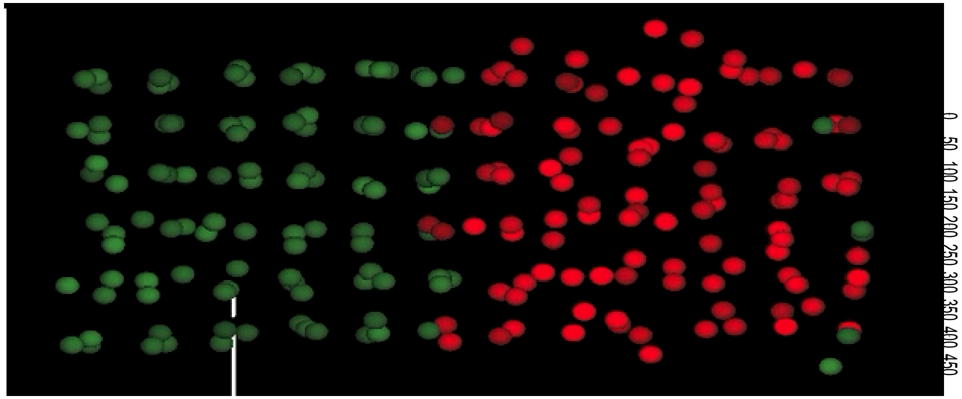
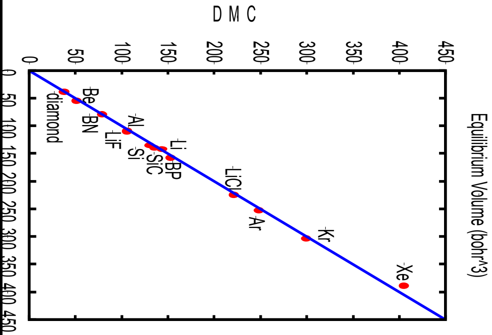
SAND2013-6113C

*Exceptional service in the national interest*







# Status of DMC for condensed phases

Luke Shulenburger

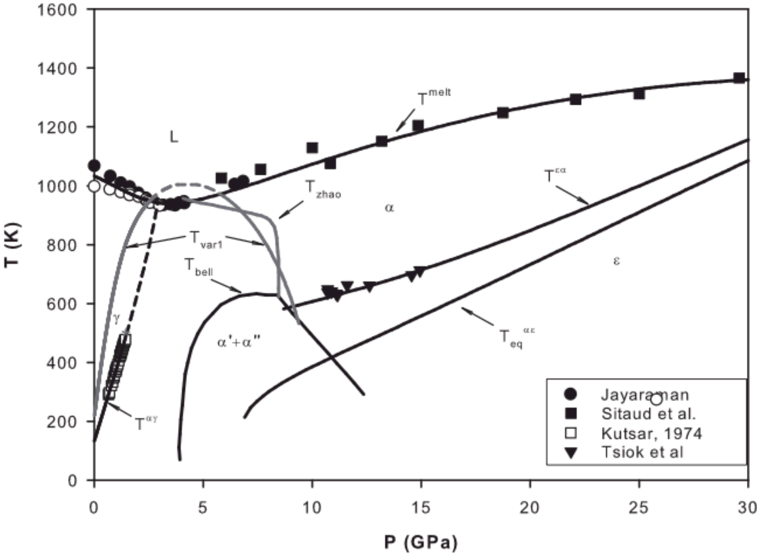
# Acknowledgments

- Thomas Mattsson
- Jeongnim Kim
- Kyle Cochrane
- Mike Desjarlais
- DOE BES
- Sandia high performance computing and ACES

# Goal is to understand properties of a wide variety of materials under pressure

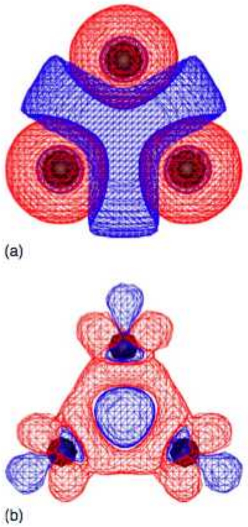
- Van der Waals interactions
- Localization vs delocalization
- Kondo physics
- Charge transfer
- Chemical Reactions

Cerium Phase diagram



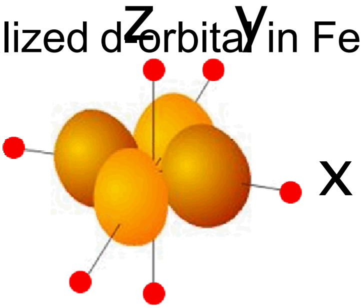
Elkin et al. PRB 84, 094120 (2011)

Xe isosurfaces



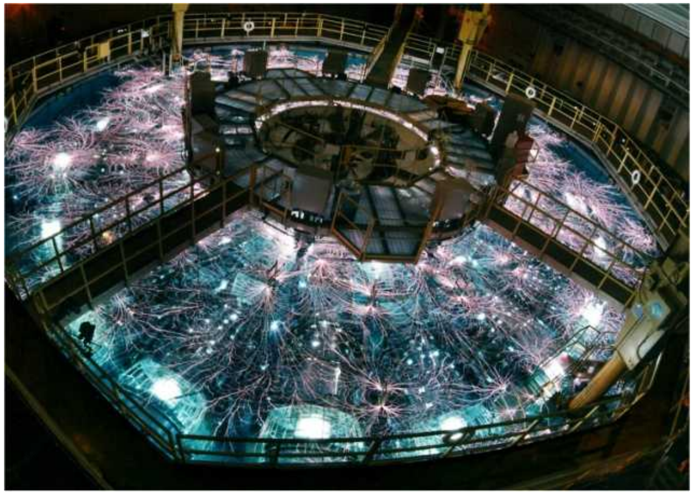
Tkatchenko et al PRB **78**, 045116 (2008)

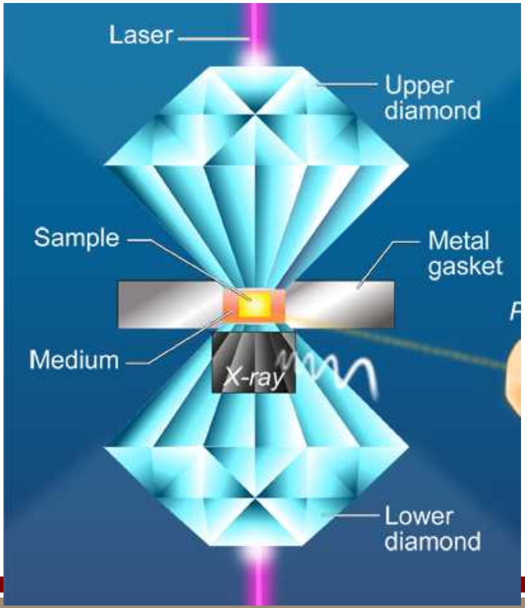
Localized d orbital in FeO



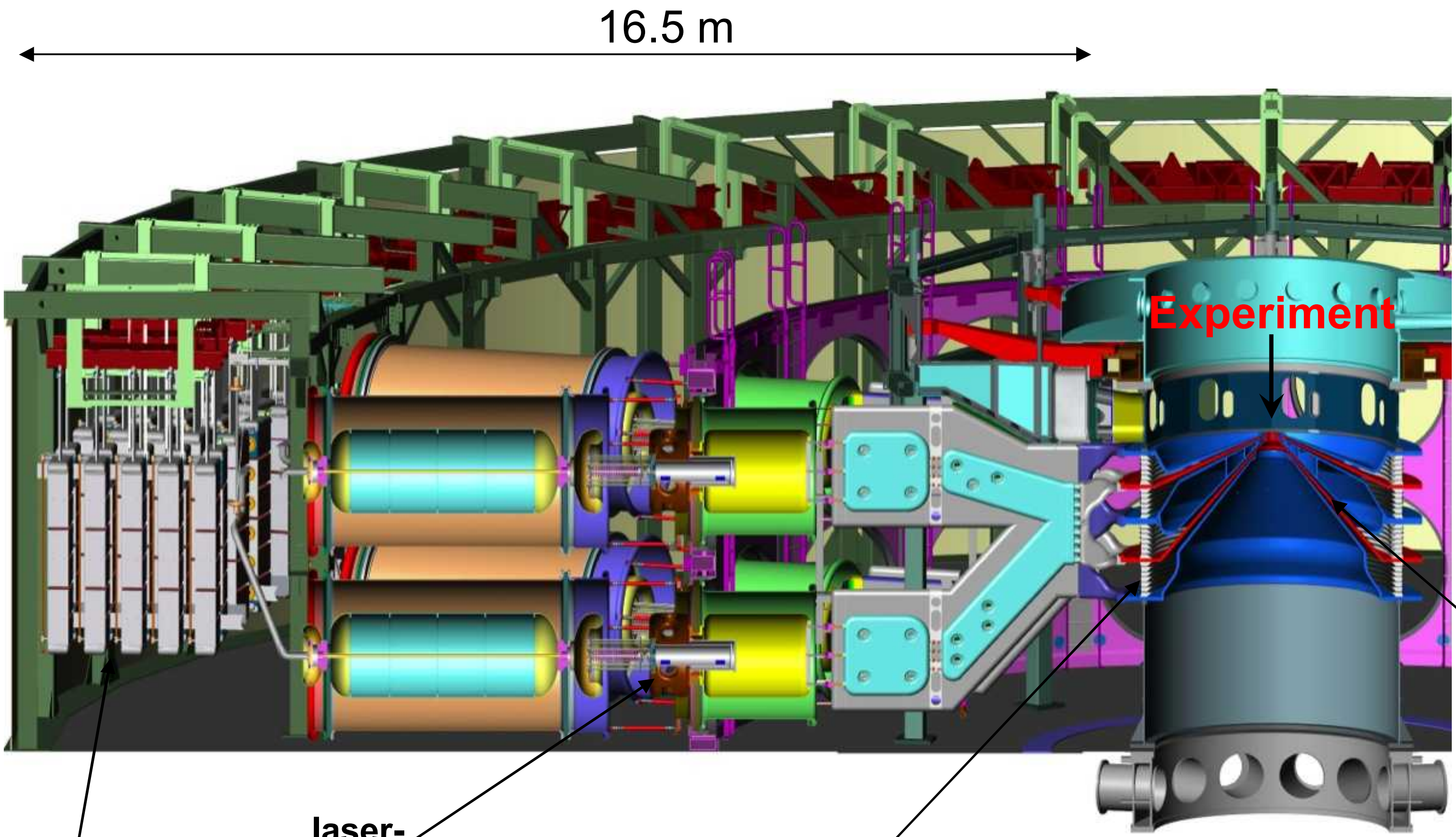
$e_g$ orbital with surrounding oxygen ions

# Techniques to probe materials at extreme conditions





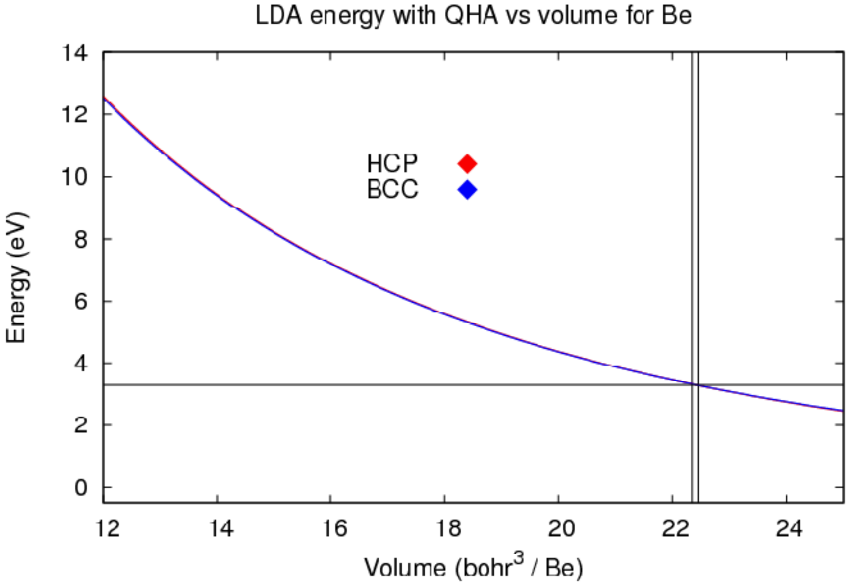
# The Sandia Z Machine

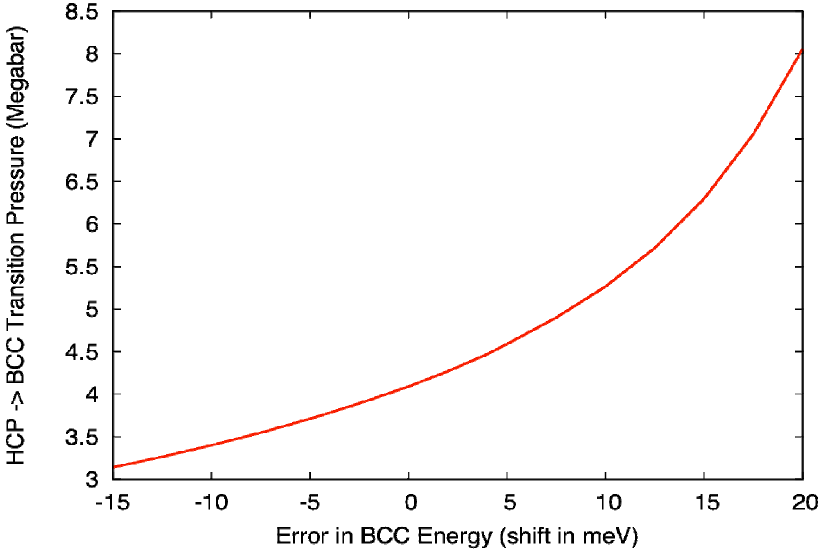


22 MJ stored energy
~26 MA peak current
~100-700 ns rise time

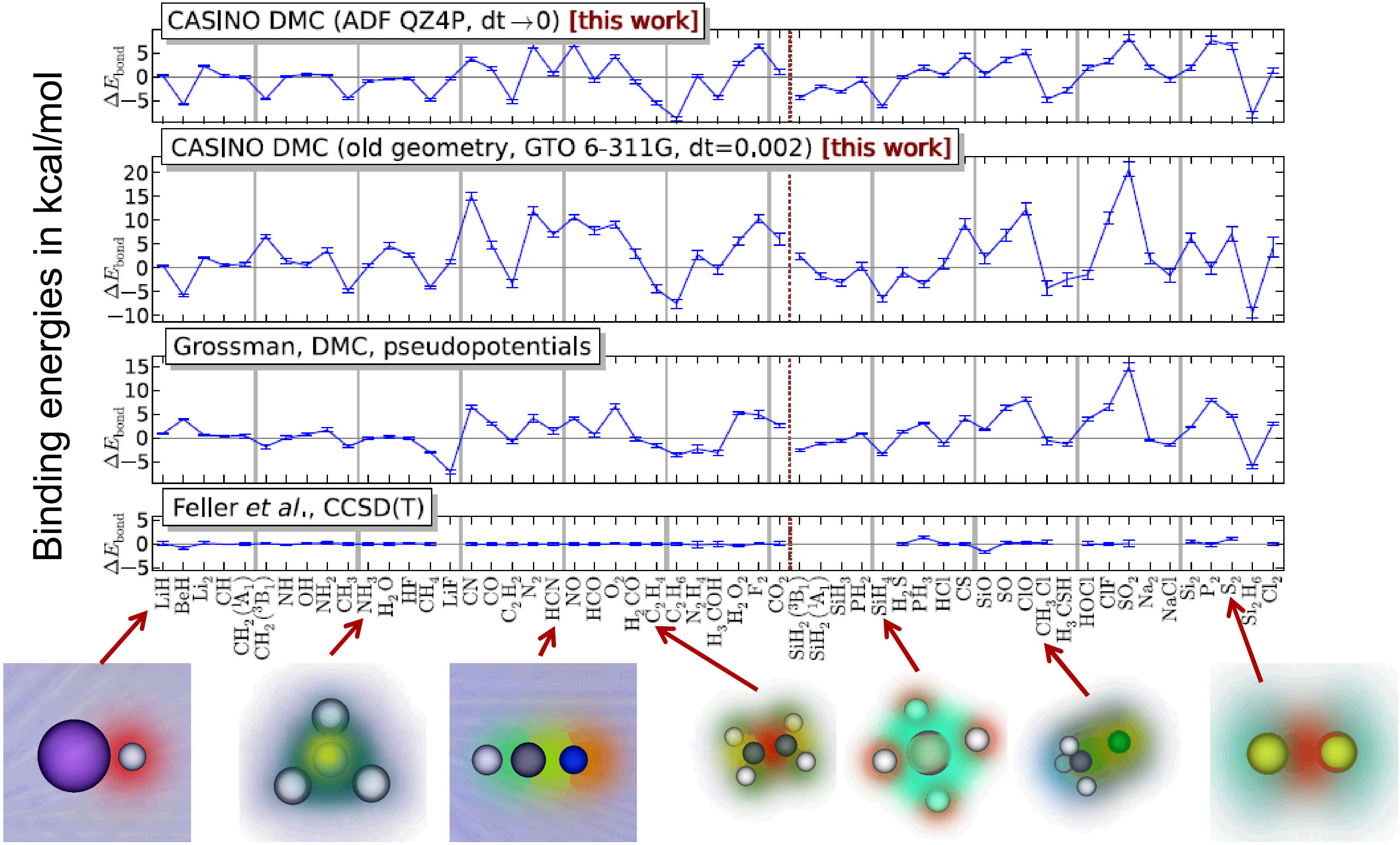
# EOS poses a stringent challenge for calculations

- Calculate Be HCP-> BCC phase transition pressure with LDA+QHA
- What is sensitivity of transition?
  - Make constant shift of $E_{HCP}(V)$
- Tansition pressure changes from 350 Gpa to 525 Gpa with a 1 kcal/mol shift
- Zero point energies were an order of magnitude larger
- Chemical Accuracy is not good enough!





# DMC may allow required accuracy

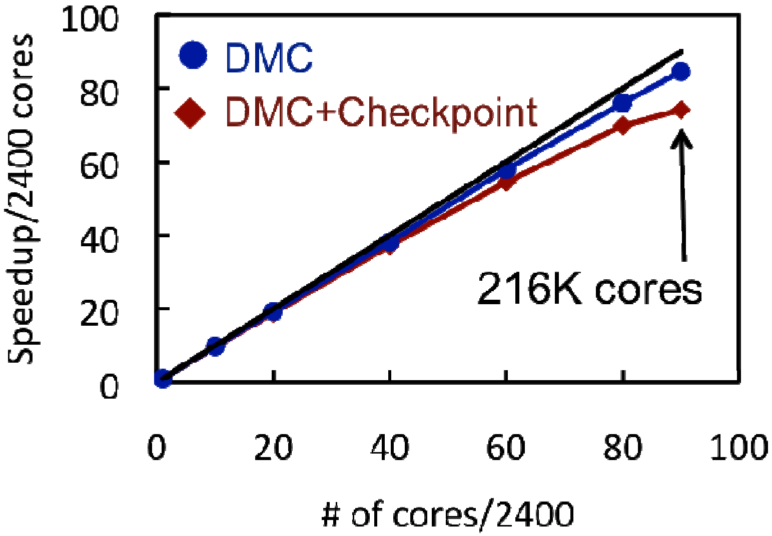


- from Nemec et al, JCP. **132**, 034111 (2010)

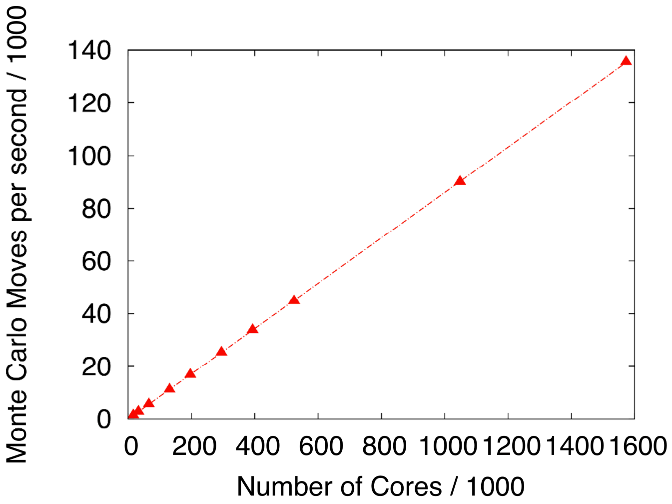
# QMCPACK – Massively Parallel QMC

- 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

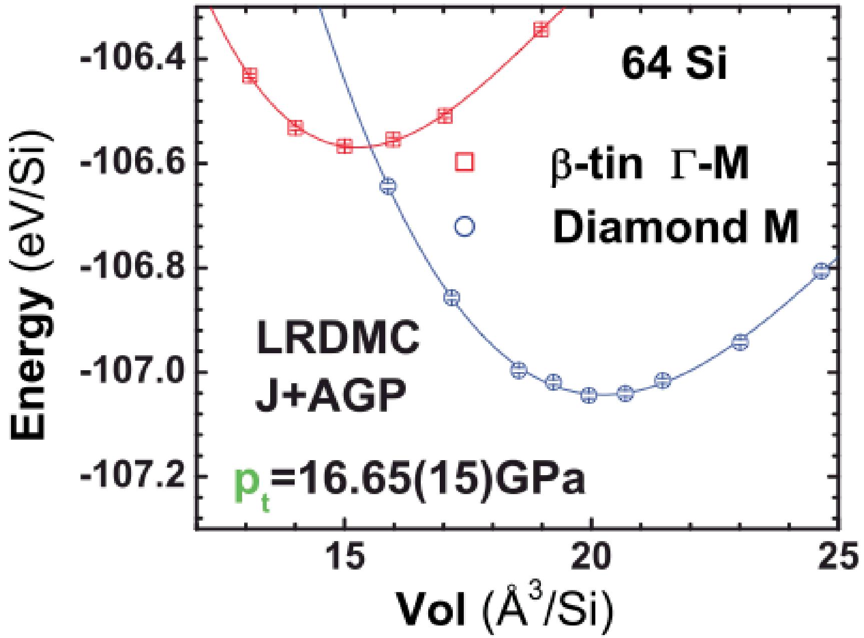


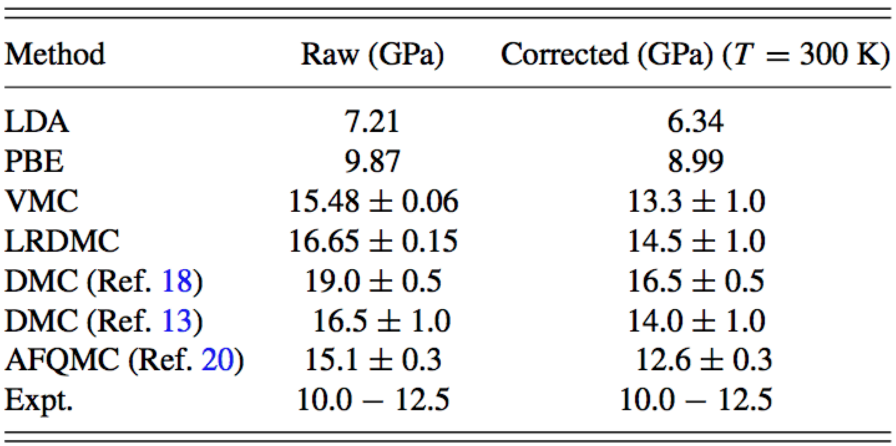
# DMC is not as mature as DFT

- 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



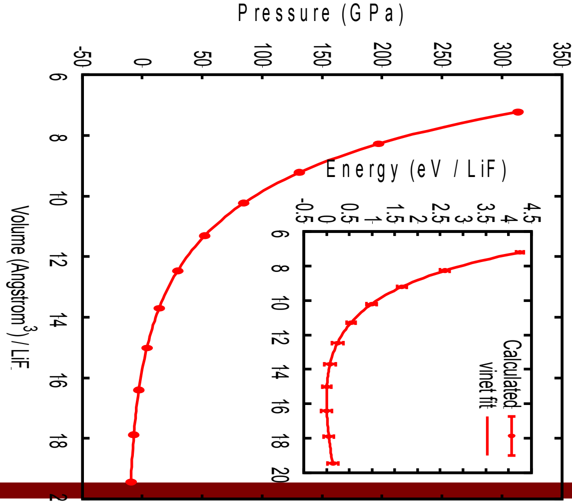


| Method | Raw (GPa) | Corrected (GPa) ($T = 300$ K) |
|---|---|---|
| LDA | 7.21 | 6.34 |
| PBE | 9.87 | 8.99 |
| VMC | 15.48 ± 0.06 | 13.3 ± 1.0 |
| LRDMC | 16.65 ± 0.15 | 14.5 ± 1.0 |
| DMC (Ref. 18) | 19.0 ± 0.5 | 16.5 ± 0.5 |
| DMC (Ref. 13) | 16.5 ± 1.0 | 14.0 ± 1.0 |
| AFQMC (Ref. 20) | 15.1 ±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

Sorella et al. PRB 83, 075119 (2011)

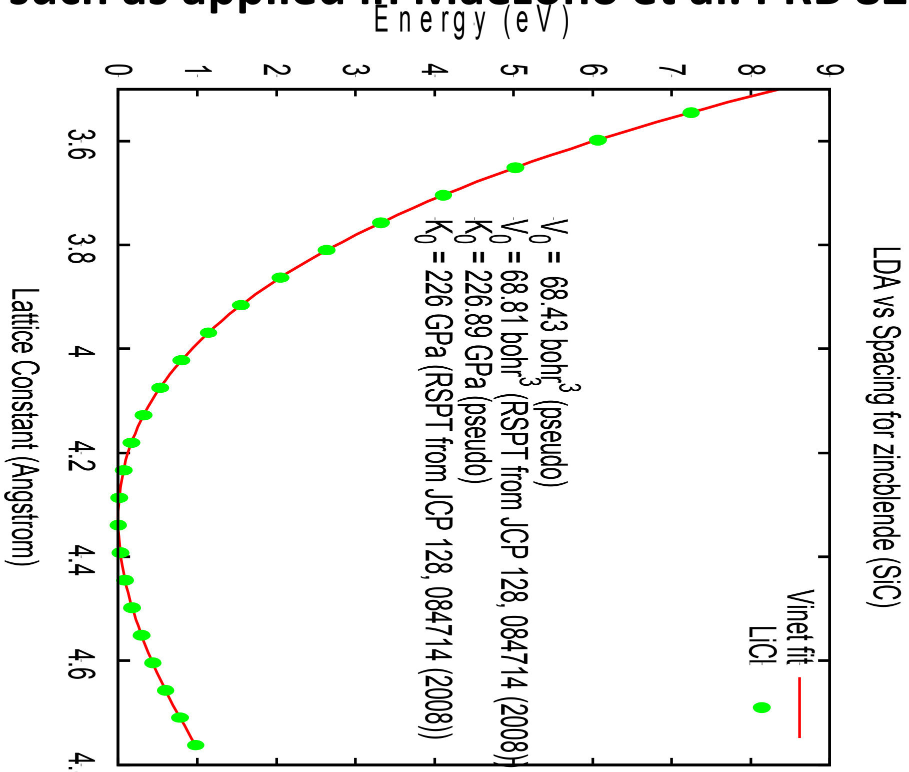
# Test approximations on a suite of solids

- 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



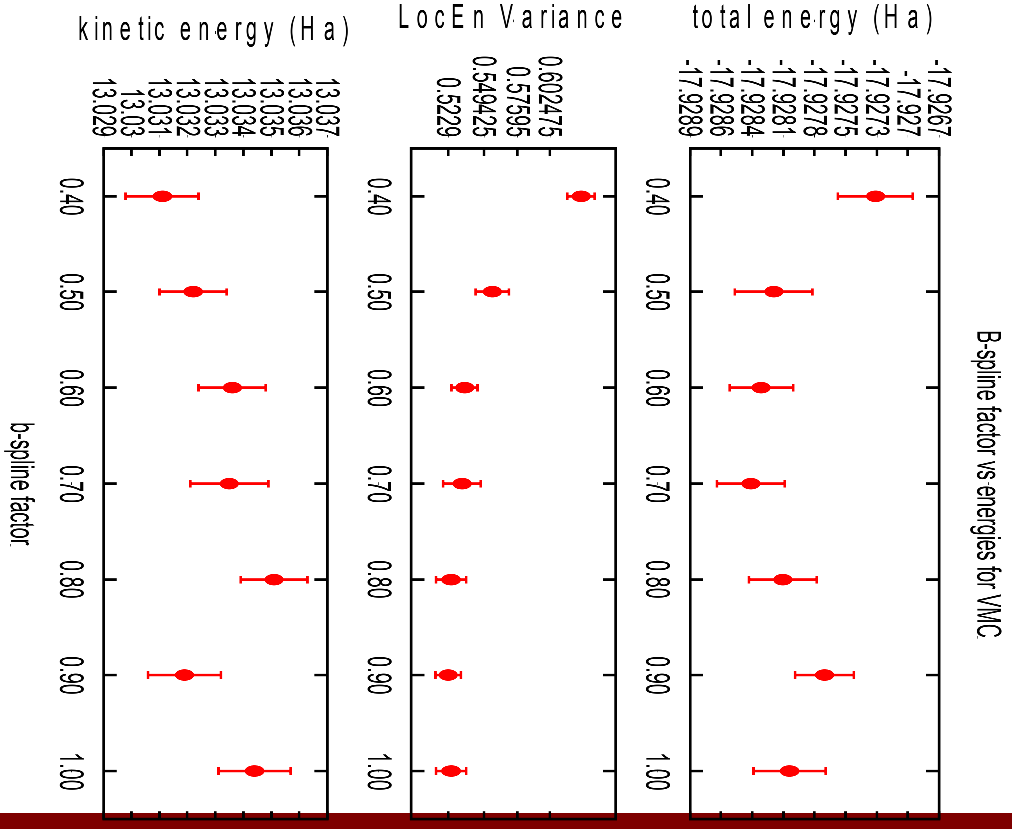
# Pseudopotential Details

- **LDA pseudopotentials constructed with OPIUM**
- **Compared to either LAPW calculations with elk or LMTO calculations with RSPT (Mattsson et al. JCP 128, 084714 (2008))**
- **Bulk modulus and equilibrium volume nearly same to minimize corrections such as applied in Maezono et al. PRB 82, 184108 (2010)**



# Convergence of technical parameters

- **Tests performed for moderate size supercell at 2 volumes**
- **Time step, b-spline spacing and twist averaging converged to within meV**
- **Finite size convergence achieved when change to larger supercell produced same energy shift in ambient and high pressure calculations**



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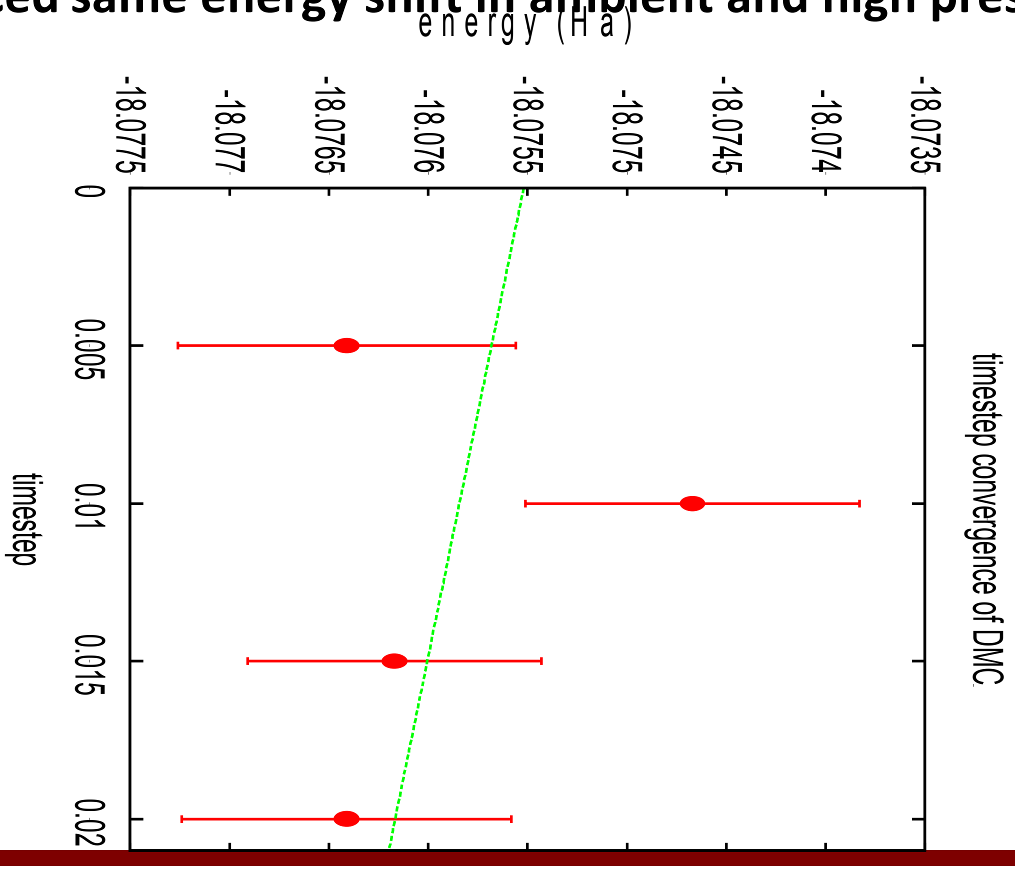

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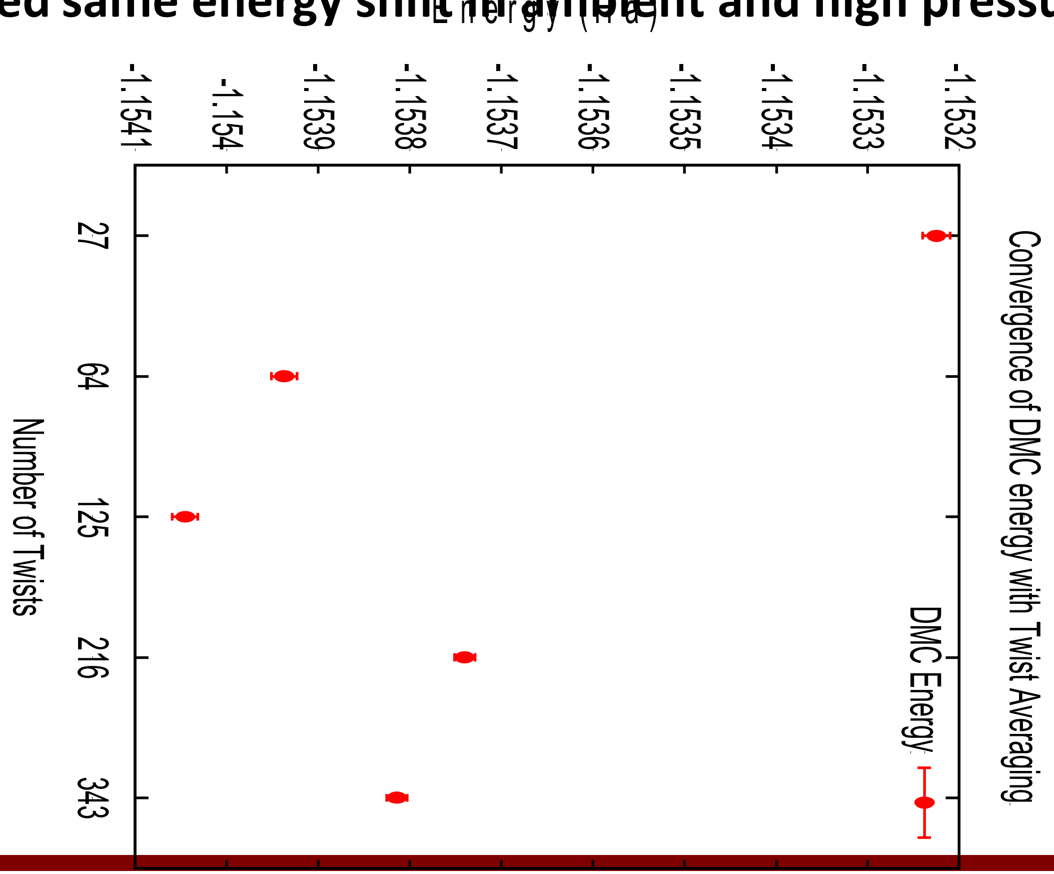
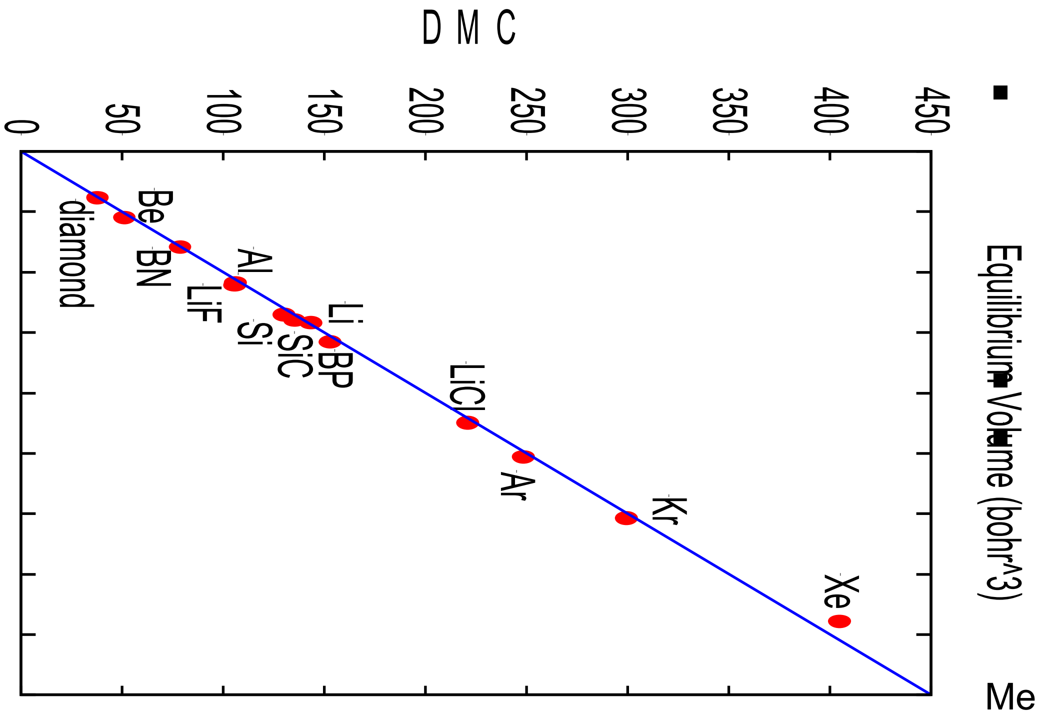


# First ever extensive benchmarks of Quantum Monte Carlo for condensed matter

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

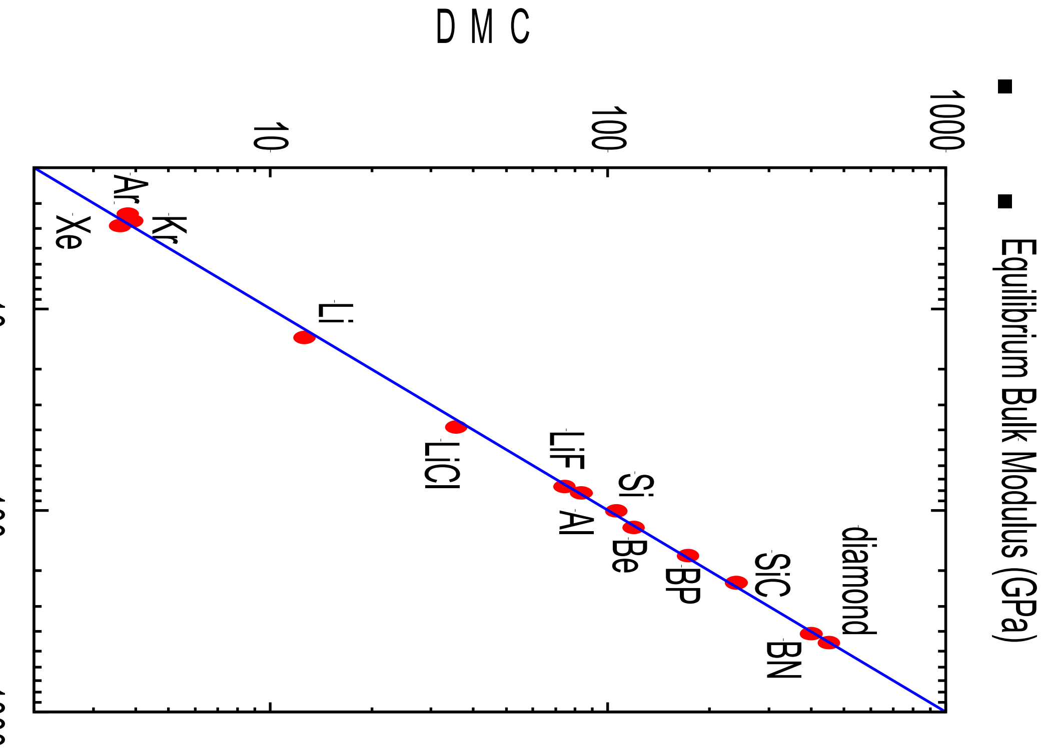


- Materials span a factor of 10 in equilibrium volume
- Four types of bonding are included
  - Ionic
  - Covalent
  - Metallic
  - Van der Waals
- Lattice Constants within ~0.9%
- This provides a new baseline procedure for a QMC calculations

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**

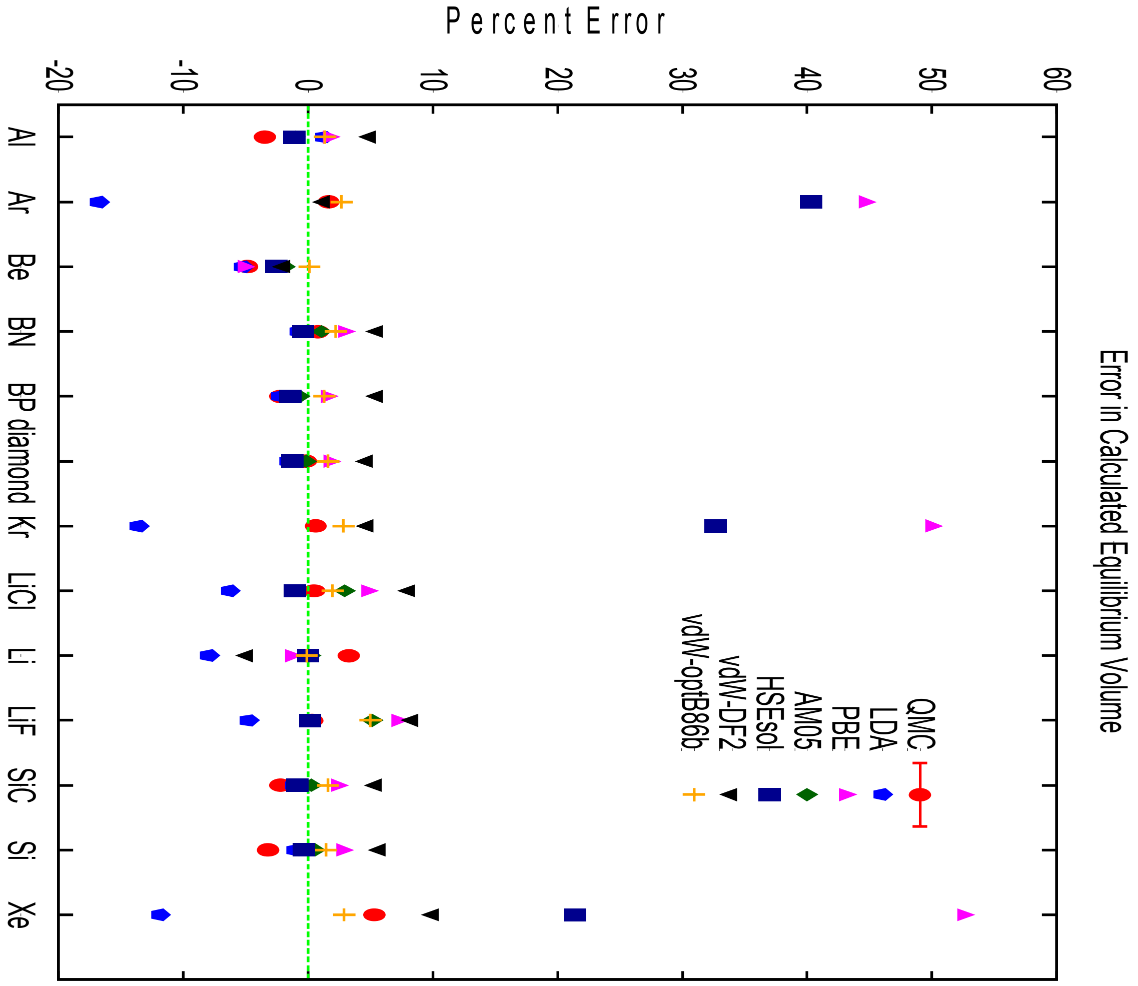


- Bulk modulus spans over 3 orders of magnitude
- This provides a new baseline procedure for a QMC calculations

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**



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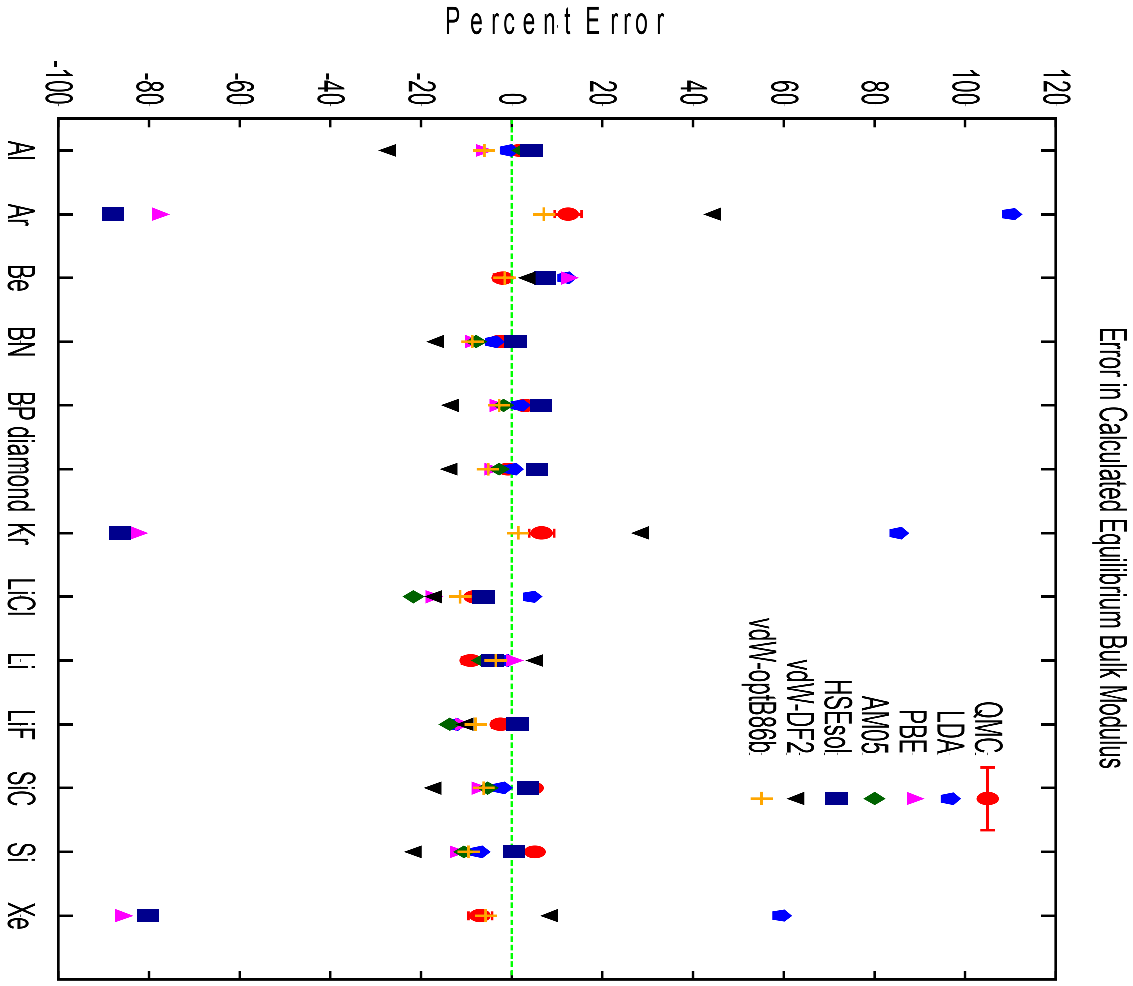
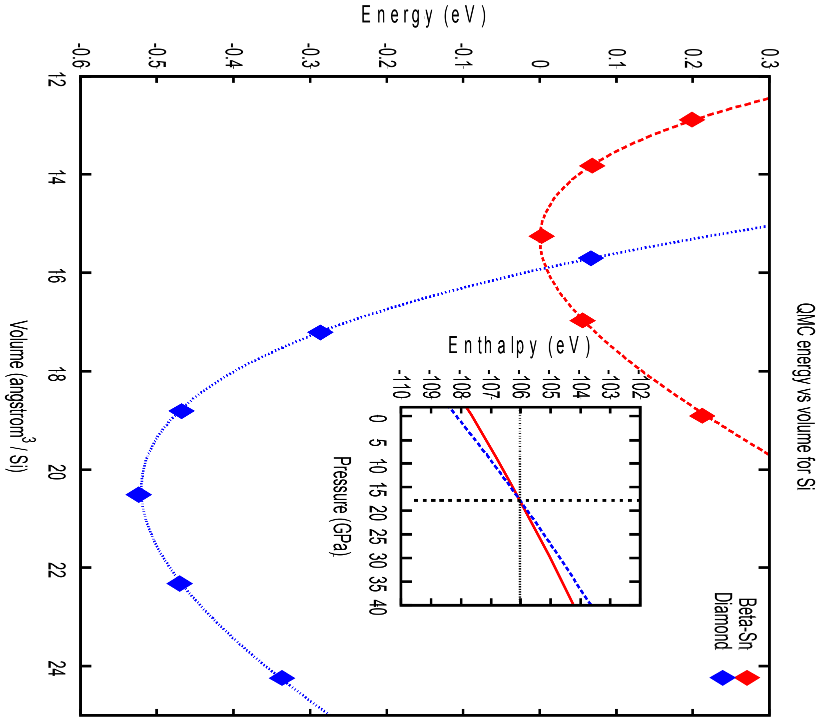


# Si Phase transition revisited:
## *Utilizing methodology from benchmark fares little better*

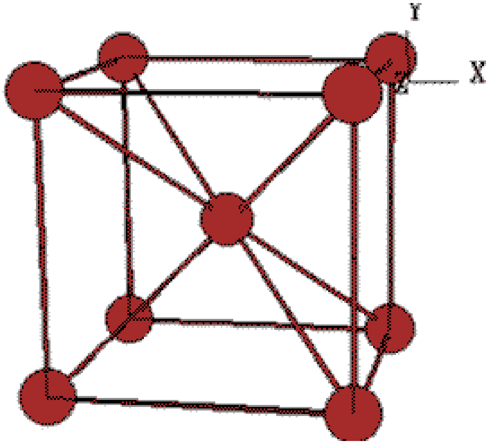
- **Use DFT based pseudopotential**
- **Extensive twist averaging for Fermi surface**
- **Chiesa correction for kinetic energy and MPC for potential**
- **Equilibrium properties are worse than reported by other groups**
  - Equilibrium density 2% too small
  - Bulk Modulus 5% too large
- **Phase Transition pressure**
  - 17.8 GPa (5-7.8 GPa too large!)

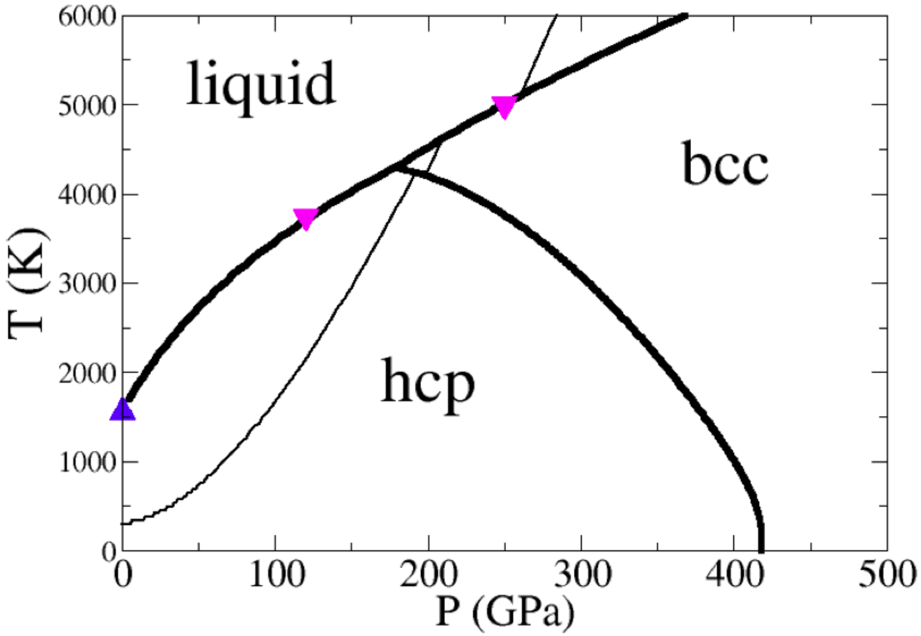


# Study simpler system to isolate errors:

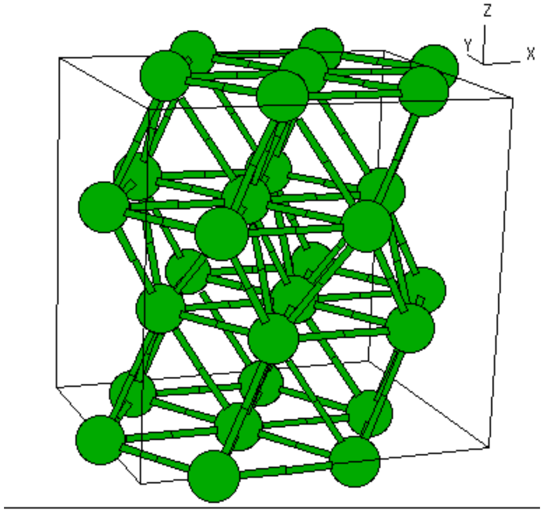
*Be HCP -> BCC phase transition*

- 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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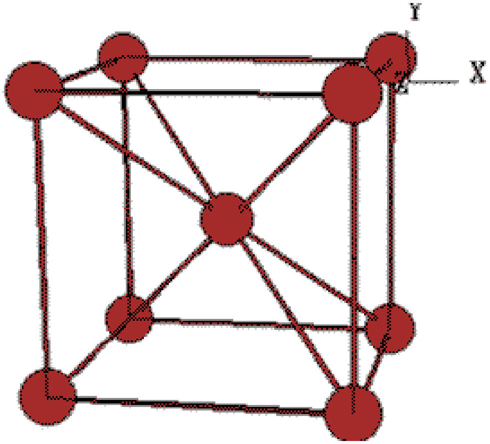
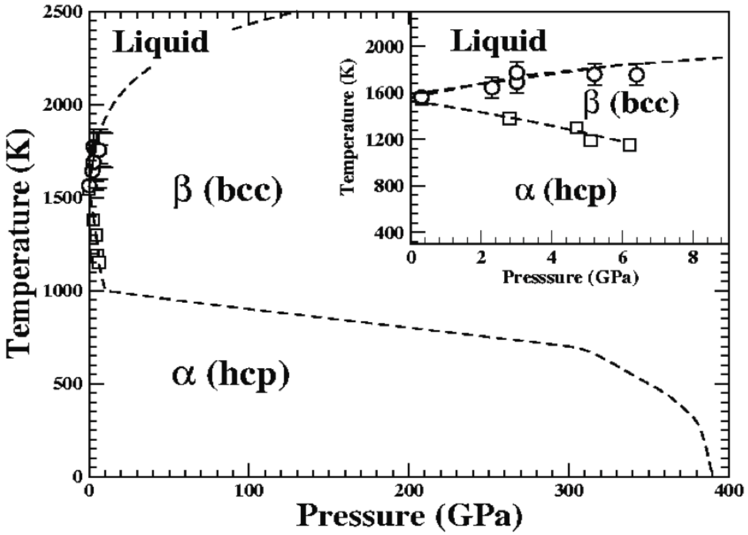
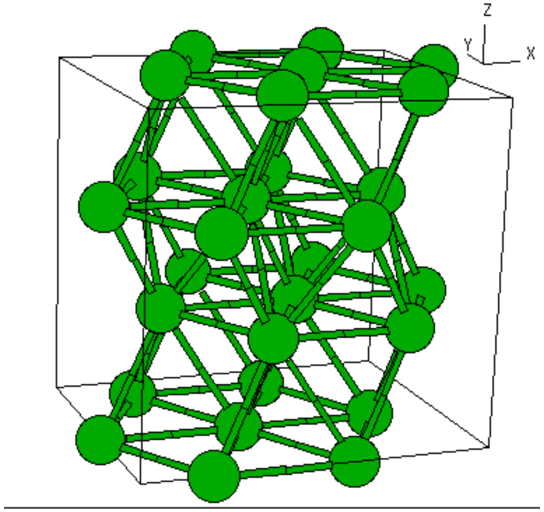




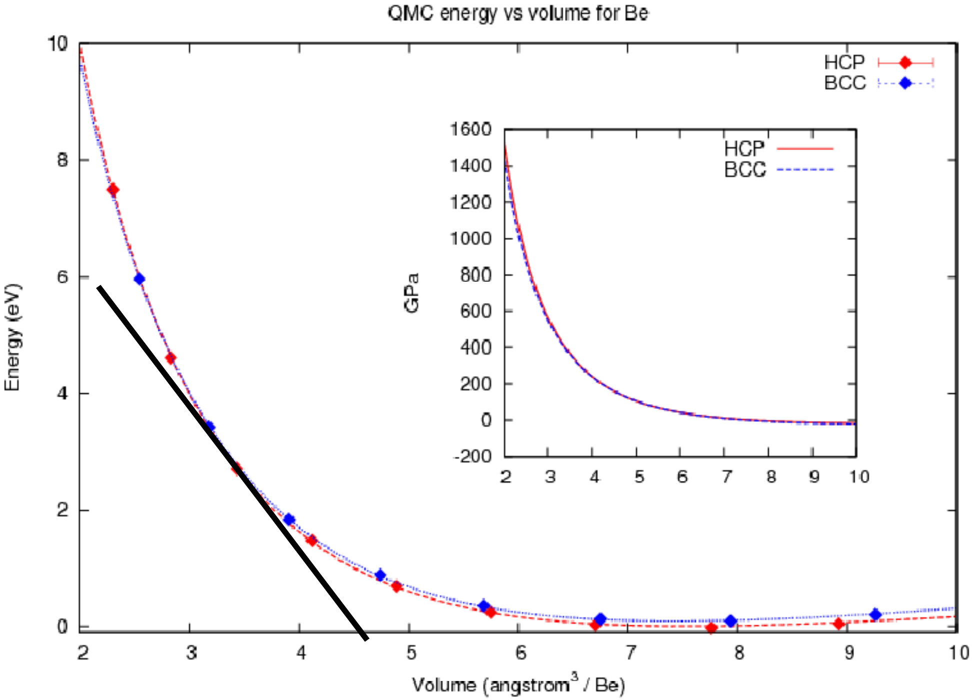


Rober and Sollier. J. Phys. IV France **134**, 257 (2006)

# Study simpler system to isolate errors:

## *Be HCP -> BCC phase transition*

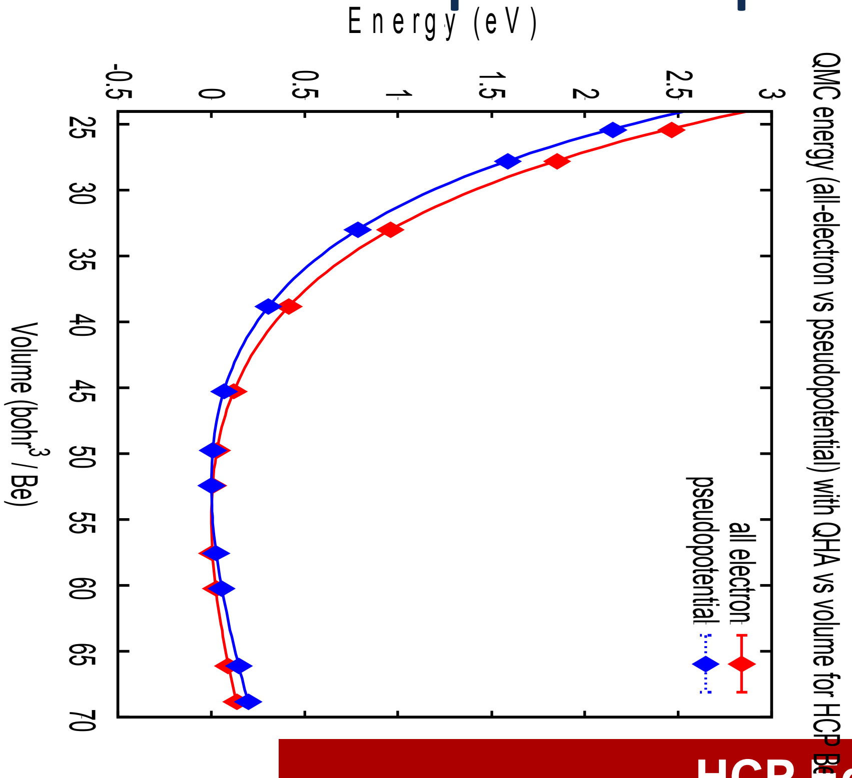
- **Equation of state is fit using Vinet form**
  - More crucial because values have statistical errors
- **Casula t-move formalism employed for pseudopotentials**
- **Phase transition occurs at > 635 GPa**
  - Significantly higher than DFT result ~ 390 GPa



**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


QMC energy (all-electron vs pseudopotential) with QHA vs volume for HCP Be

- **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**

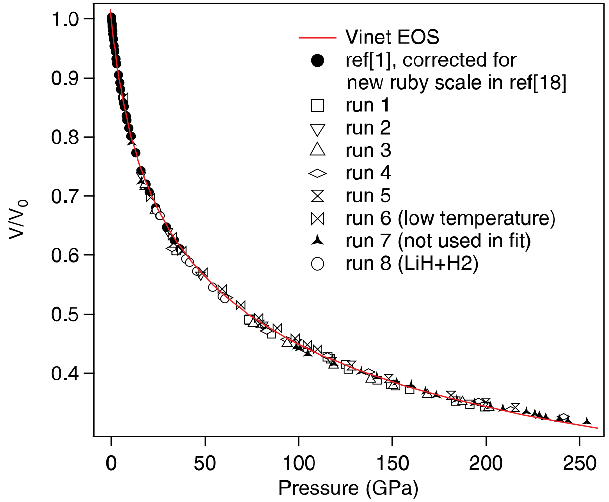
| | QMC | All Electron QMC | Exp |
|---|---|---|---|
| c/a | 1.569 +/- 0.004 | 1.569 +/- 0.004 | 1.568 |
| $V_0$ (angstrom^3) | 7.746 +/- 0.078 | 8.123 +/- 0.006 | 8.117 |
| Bulk Modulus (GPa) | 124 +/- 2 | 115.7 +/- 1.5 | 116.8 |

# Accuracy of all electron methodology holds for another light nuclei phase transition

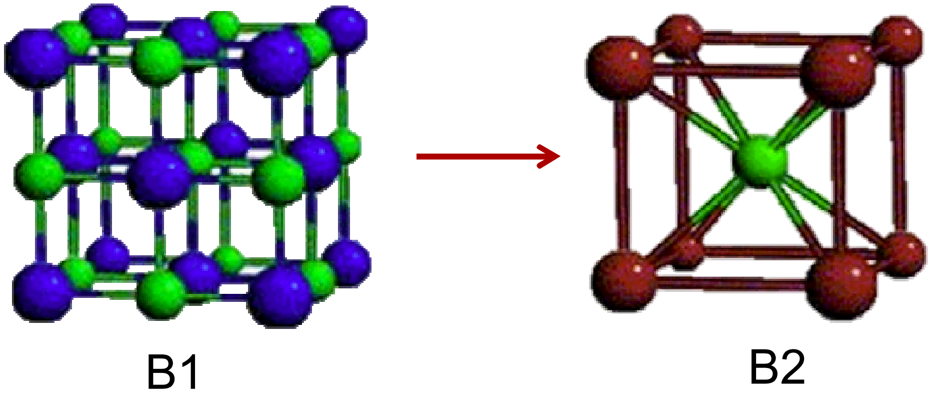
- **Calculate LiH transition from B1 to B2 phase**
- **Ambient (B1) phase in excellent agreement with experiment**
- **Phase transition pressure 337 GPa**
- **DFT (LDA) calculations 308 Gpa**
- **Complements DAC experiments which top out near 250 GPa**

**B1 Equilibrium Parameters**

| | QMC | Exp |
|---|---|---|
| Lattice Constant (angstrom) | 4.074 +/- 0.002 | 4.08 |
| Bulk Modulus (GPa) | 32.2 +/- 0.4 | 33.1 +/- 0.3 |
| B’ | 3.64 +/- 0.05 | 3.64 +/- 0.05 |



Lazicki et al. PRB, **85**, 054103 (2012)



# Minimizing the pseudopotential approximation will have the largest impact on DMC calculations of solids

- **Phase transitions under pressure provide sensitive test of DMC**
- **Calculations using high quality DFT pseudopotentials have mediocre accuracy**
- **All electron calculations of Be and LiH give extremely accurate properties for equilibrium phases**
- **All electron phase transition pressures agree with available experiments and are comparable to best DFT based answers**
- **All electron calculations are not a feasible proposition for many applications**
- **Reducing the pseudopotential approximation should be the highest priority for the calculation of solids with DMC**

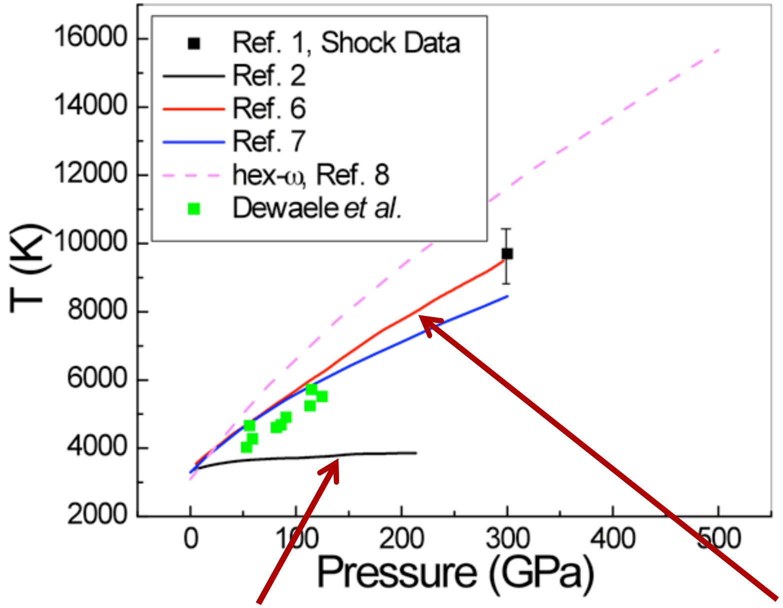
# Moving to higher temperatures

- **High pressure low temperature conditions are quite rare in the universe**
- **Zero temperature behavior sets the foundation, but does not constrain all of an equation of state**
- **Melt boundaries, isentropes, adiabats, critical points etc are all of interest experimentally**
- **No general path for high temperature properties from DMC**
  - Combine with another method
  - Free energy decomposition: $F(V,T) = F_c(V) + F_i(V,T) + F_e(V,T)$
  - Thermodynamic integration

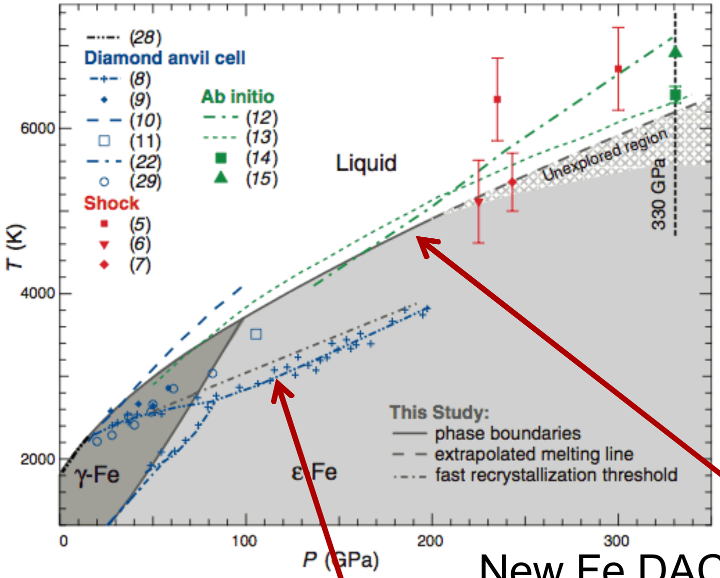
# Melt boundaries are particularly challenging

- Target recent discrepancies in melt curves under pressure
- Early DAC experiments may have encountered a variety of difficulties
  - Where available, shock determinations of melting often suggest a much steeper melt curve
  - Increased reactivity at high temperature and pressure can lead to chemical reactions that lower melt curve
  - Fast recrystallization caused by different absorption profiles of the solid and liquid can also lead to lowered determination of melting profile

Ta melt curve



Fe melt curve



New Fe DAC Melt cu

Old Ta DAC Melt curve

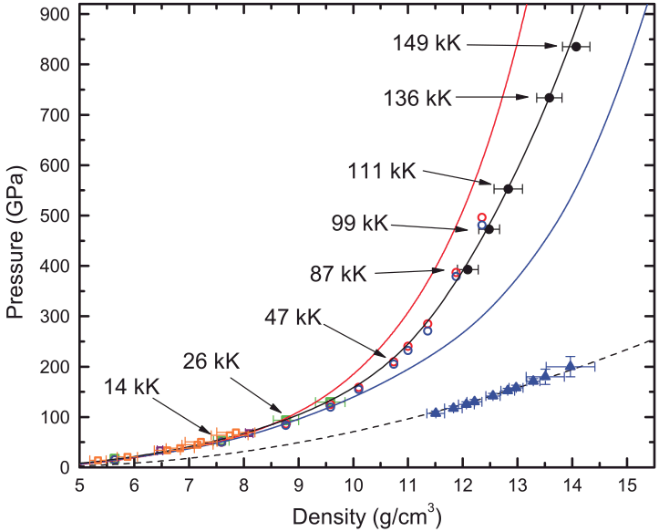
New Ta DAC Melt curve

Old Fe DAC Melt curve

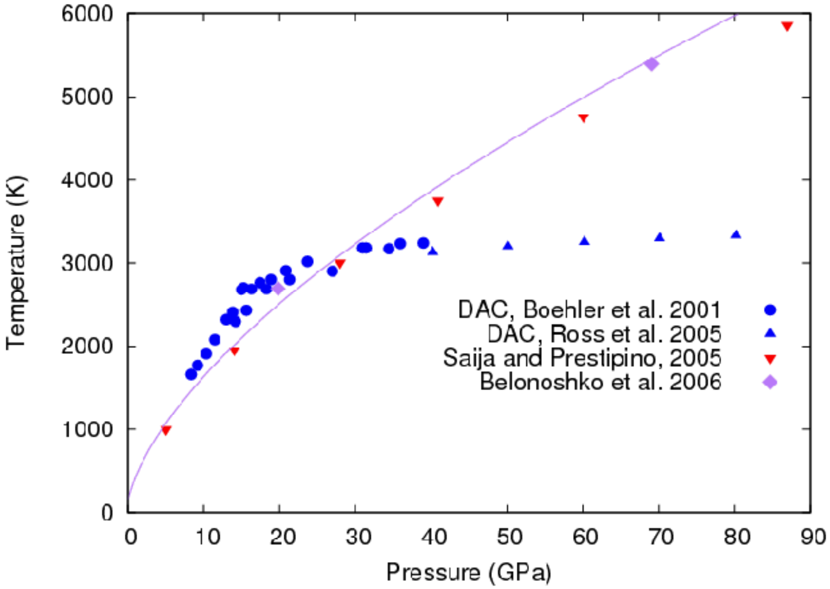
Klug, Physics. **3**, 52 (2010)

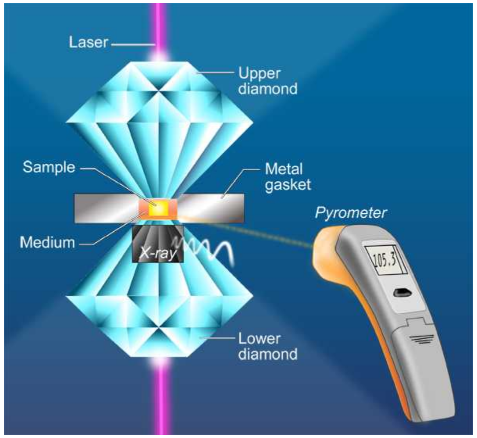
# Case Study: xenon melt transition

- Closed shell insulator at ambient conditions
- Under static compression
  - FCC -> HCP Phase transition
  - Isostructural insulator to metal transition
- Hugoniot well characterized
- Liquid phase may exhibit anomalous behavior
  - Very narrow temperature range at ambient pressure
  - Potentially flat melt curve at moderate pressures



Root et al. PRL **105**, 085501 (2010)

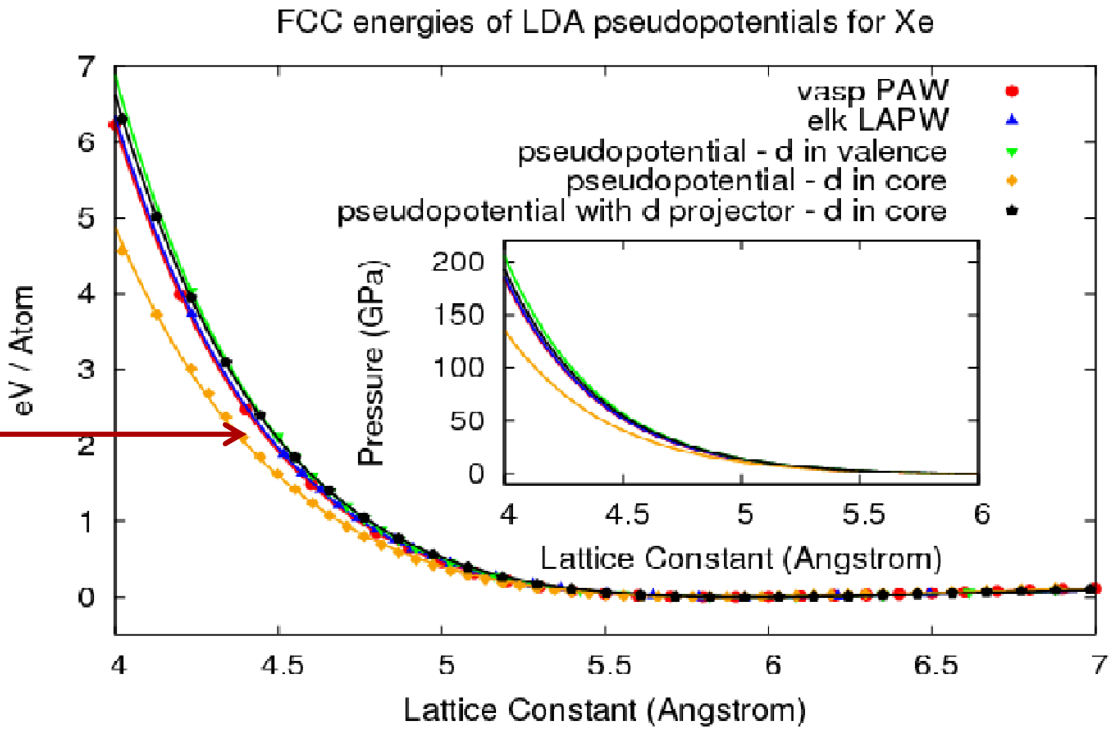




Klug, Physics. **3**, 52 (2010)

# Pseudopotential poses a particular challenge for accurate DMC calculations

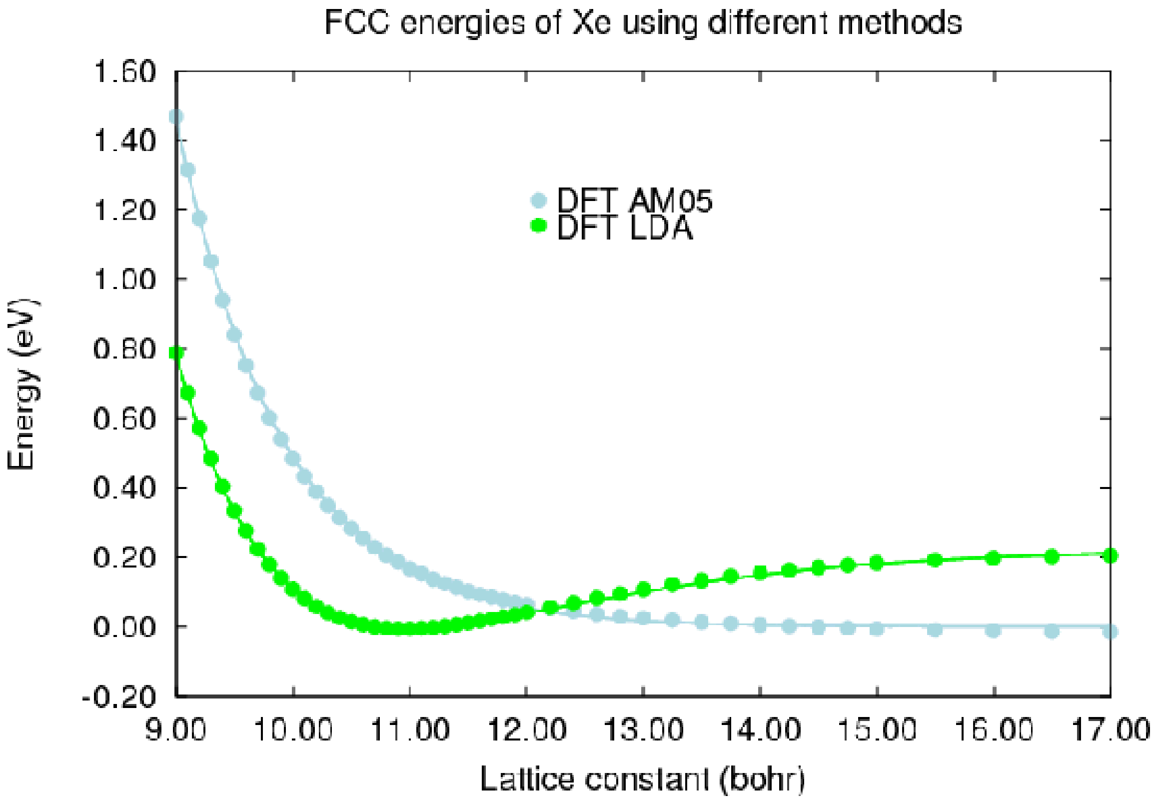
- **Validated norm conserving Xe pseudopotentials not widely available**
- **D-states well removed from valence, but d-projector is crucial**
  - **Increasing d-hybridization suggested as cause of flat melt line**
    - *Ross et al. PRL 95. 257801 (2005)*



~0.5 eV / Xe difference at 70GPa

# Fixed node approximation and DFT Functional

- **FCC equation of state**
  - **LDA → no long range correlation, but self interaction in low density regions**
  - **AM05 → subsystem based functional, van der Waals is completely absent**



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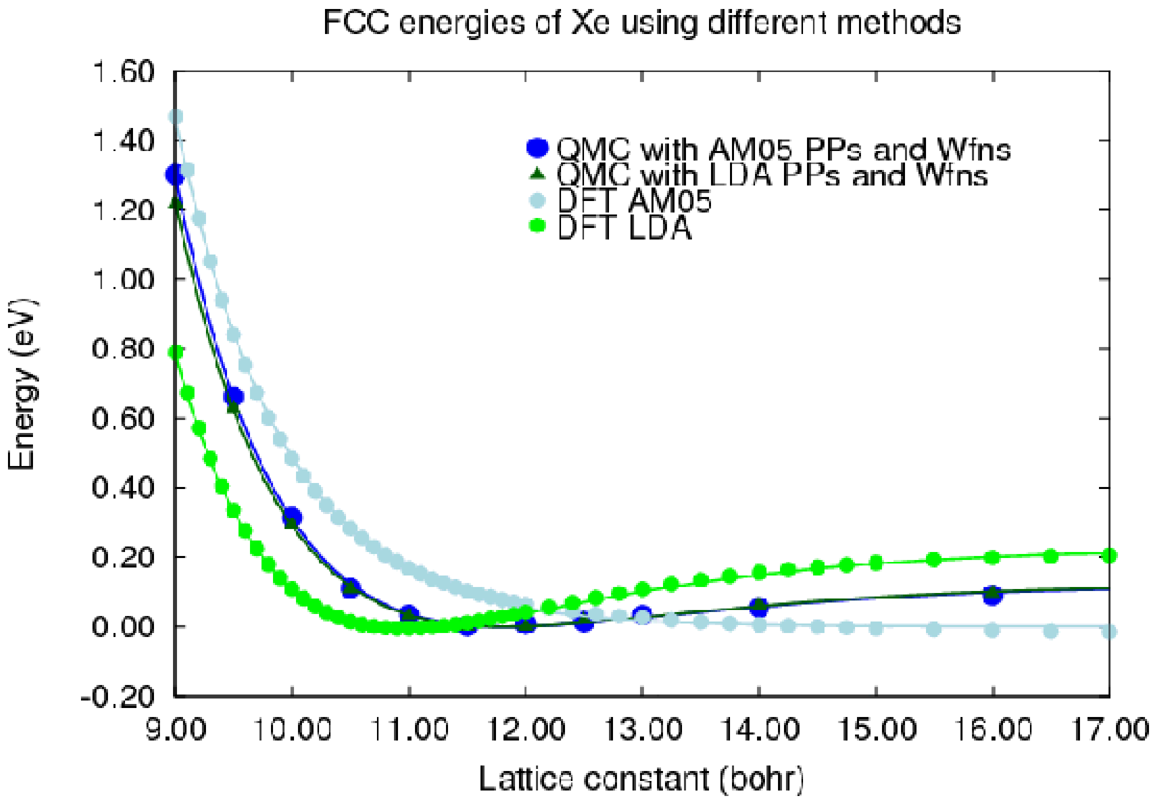
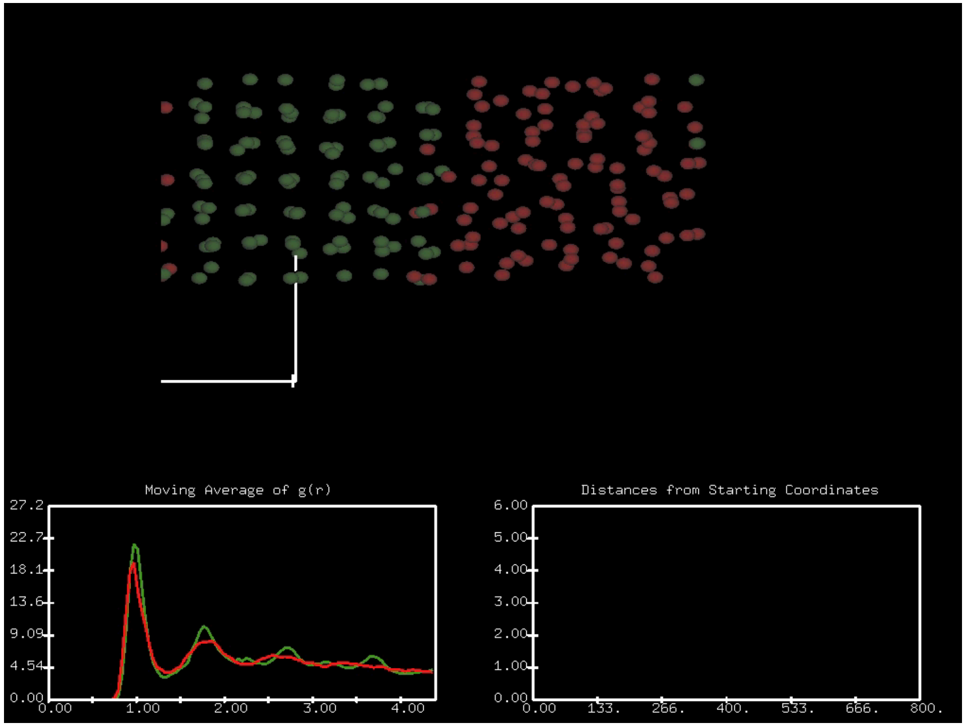
  - **LDA → no long range correlation, but self interaction in low density regions**
  - **AM05 → subsystem based functional, van der Waals is completely absent**
  - **DMC with nodes and pseudopotentials taken from above calculations**
    - *Very small dependence on DFT trial wavefunction*



# Difficult to determine free energy directly:
## *Determine relative free energy of phases within QMD*

- Place solid and liquid in contact with each other
- Run at different temperatures or starting energies and watch phase boundary
- Relative heat capacities and enthalpy of melting determine range of phase coexistence



- Melt at 5800 K
- Freeze at 5400 K

# Thermodynamic integration to map to DMC free energies

- Calculate the change in free energy between different ensembles
- There are two approaches, a one shot formula or a perturbation series

$$
\begin{aligned}
\Delta F &= F_2 - F_1 \\
&= -k_B T \ln Z_2 + k_B T \ln Z_1 \\
&= -k_B T \ln \sum_s e^{-\beta U_s^2} \Big/ \sum_s e^{-\beta U_s^1} \\
&= -k_B T \ln \sum_s e^{-\beta (U_s^2 - U_s^1)} e^{-\beta U_s^1} \Big/ \sum_s e^{-\beta U_s^1} \\
&= -k_B T \ln \left\langle e^{-\beta \Delta U)} \right\rangle_1
\end{aligned}
$$

$$\Delta F = \sum_{n=1}^{\infty} \frac{(-\beta)^{n-1}}{n!} \kappa_n$$

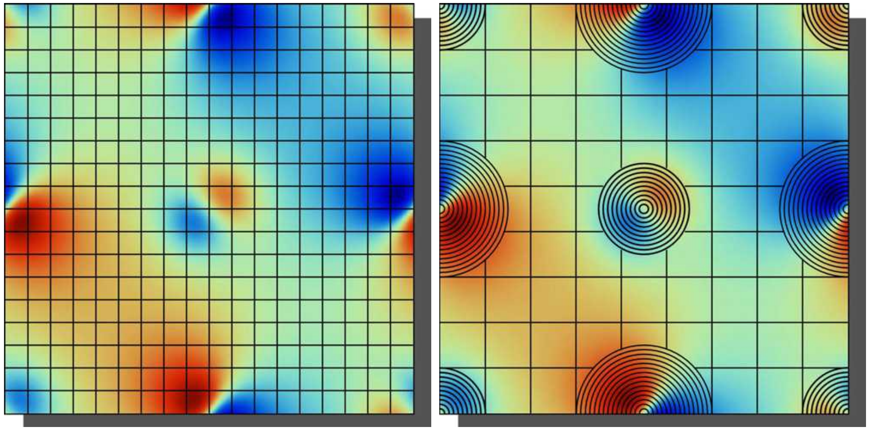
Where the $\kappa_n$ are cumulants of the energy

$$
\begin{aligned}
\kappa_1 &= \langle \Delta U \rangle_1 \\
\kappa_2 &= \langle \Delta U^2 \rangle_1 - \langle \Delta U \rangle_1^2 \\
\kappa_3 &= \langle \Delta U^3 \rangle_1 - 3 \langle \Delta U \rangle_1 \langle \Delta U^2 \rangle_1 + 2 \langle \Delta U \rangle_1^3
\end{aligned}
$$

- Comparison of the two approaches provides a rough idea of the rate of convergence of the series
- Need to calculate energy differences from snapshots

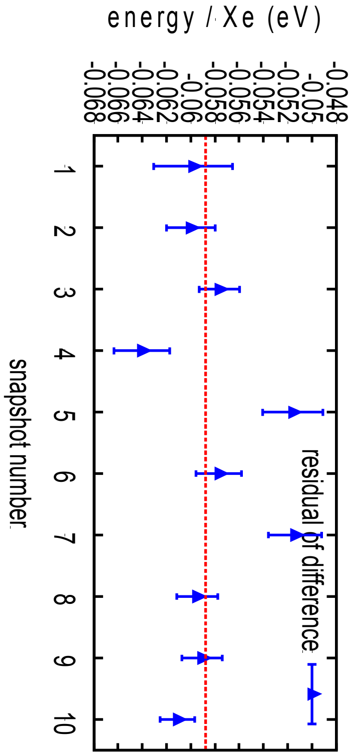
# Trial wavefunctions used for QMC

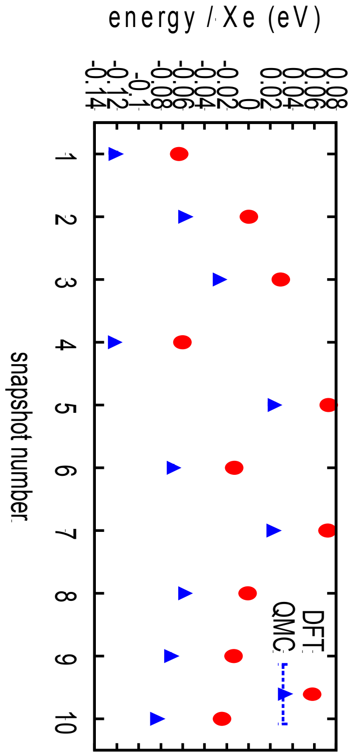
- **Use a real space representation of the wavefunction**
  - Plane waves require evaluation of each basis element for every move
  - 3D b-splines require only 64 evaluations at each point
  - Very large amounts of memory required : 96 GB / wavefunction
- **Hybrid Representation**
  - Use coarse b-spline mesh in real space
  - Radial spline near atoms
  - Wavefunctions reduced to 24 GB
  - Conversion is expensive for large systems
- **GPU port of wavefunction conversions**
  - Massive parallelism available
  - Conversion Time reduced from 10 days on 16 CPU cores to 6 hours on 4 GPUs



(a)Uniform B-spline (b)Mixed basis

# Thermodynamic integration in practice





- 10 snapshots taken from a solid QMD calculations with LDA functional
- Free energy shift from exponential:
  - -0.05947 +/- 0.00085 eV / Xe
- Terms from the perturbation series
  - 1st order: -0.05818 +/- 0.00067 eV/Xe
  - 2nd order: -0.00158 +/- 0.00023 eV/Xe
  - 3rd order: -0.00030 +/- 0.00012 eV/Xe
- Fast convergence leads to confidence in closeness of ensembles

# Two approaches to determine the shift of the melt line

- Determine the change in Gibbs free energy directly

$$\Delta T_m \approx \frac{\Delta G^{ls}}{S_{DFT}^{ls}} \qquad \Delta G \approx \Delta F - V\Delta p^2 / 2K_T$$

  - Approach from Sola and Alfe PRL **130**, 078501 (2009)
  - Some uncertainties in how to evaluate $S_{DFT}^{ls}$ and Δp

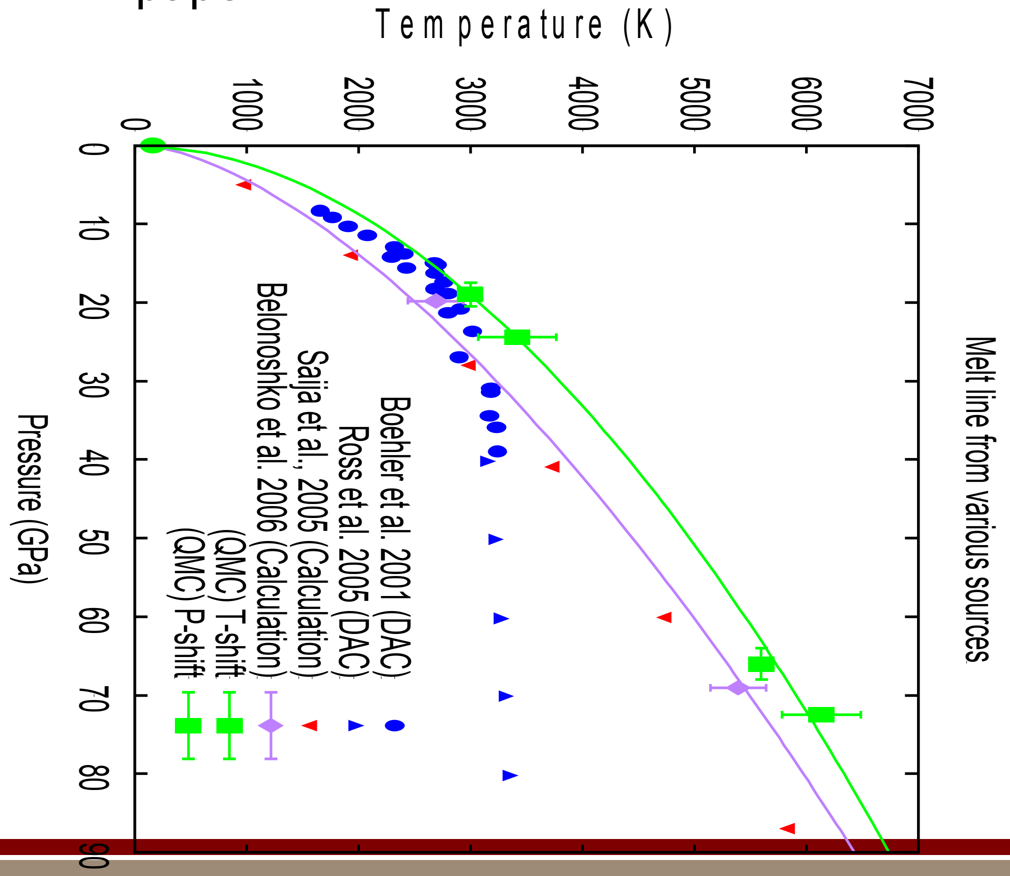
- Alternative is to work with Helmholtz free energy
  - Calculate isotherm with DFT in each phase

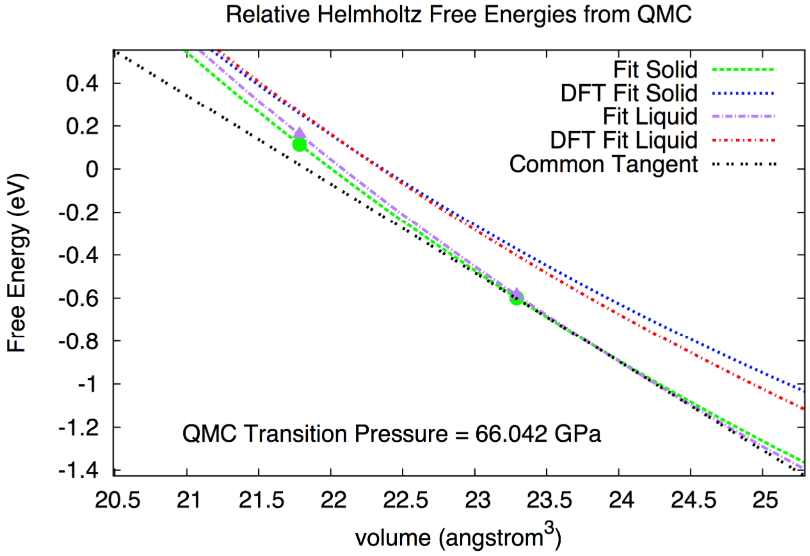
$$F = -PdV - SdT \longrightarrow dF = -\int P\,dV + C$$

  - Use pressure from two phase calculations to set relative shift between phases within DFT
  - Thermodynamic integration at multiple volumes allows for changes in slope of free energy

# QMC correction on DFT melt line

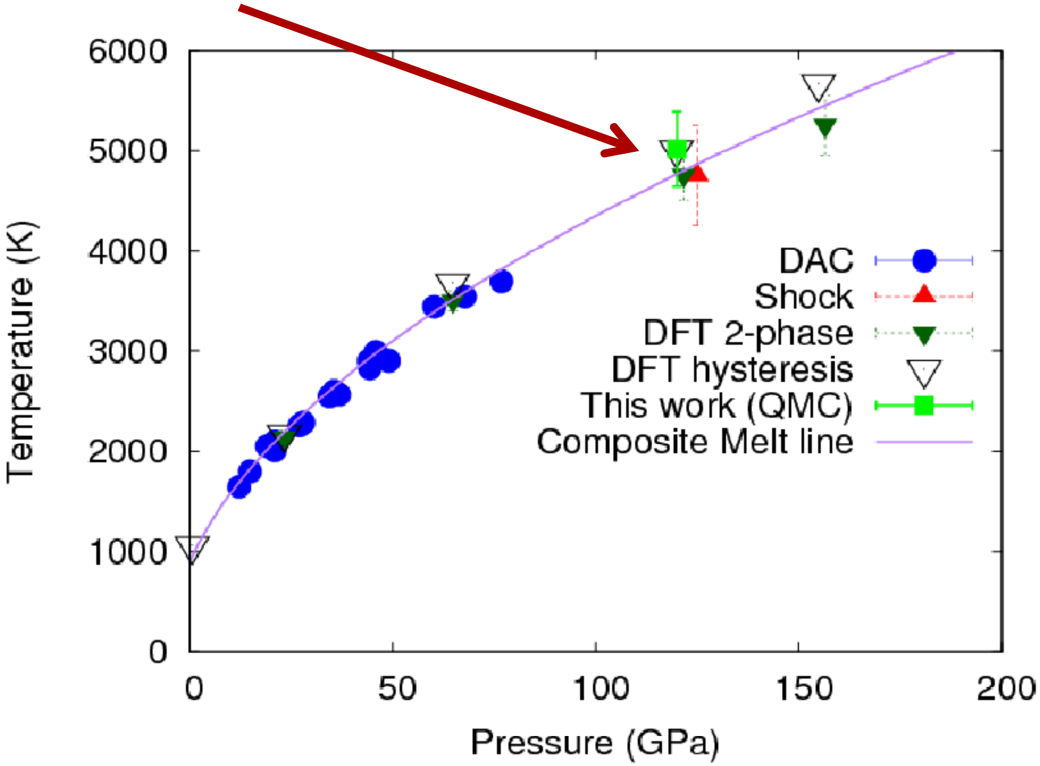
- No evidence for low melt line found by experiment
- Shifts from DMC are a similar magnitude as those found in the iron paper





# Validation of method: Melting of aluminum

- Shock and DAC melt exhibit a consistent trend
- DFT (2 phase approximation) accurately reproduces melt curve
- Thermodynamic integration from DFT to QMC gives a shift of only 18 K !



# Conclusions

- **Diffusion Monte Carlo can accurately treat Xe under pressure**
  - **Pseudopotential Approximation is small**
  - **Fixed node approximation is likely a small error**
- **Accurate treatment of d-hybridization does not cause melt curve to flatten**
- **Relative energies from DFT within LDA appear to be accurate near 1 Mbar**
- **Errors in total energies from quantum MD calculations will increase melting temperature**
- **Flat melting curve from DAC should be revisited**