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Wednesday, Feb 29, 2012, Session P25, 8:00 AM

Quantum Monte Carlo applied to solids under pressure

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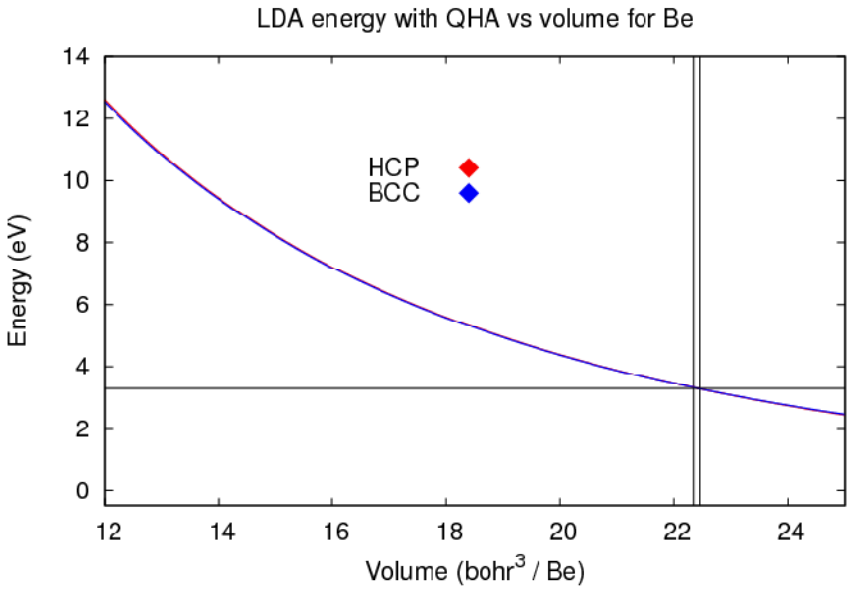
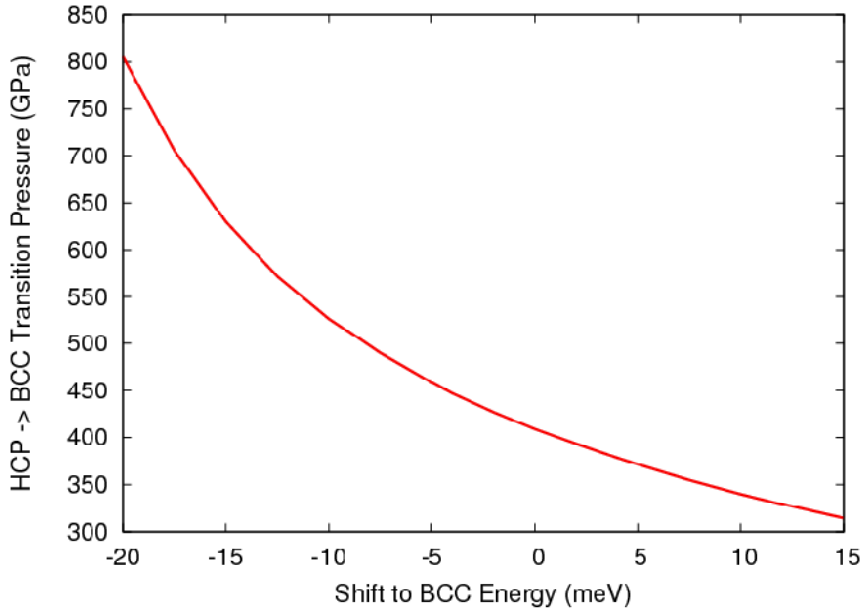
- Kyle Cochrane
- Mike Desjarlais
- Sandia high performance computing and ACES

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 $E_{BCC}(V)$**
- **Transition pressure changes from 350 GPa to 525 GPa with a 1 kcal/mol shift**
- **Chemical Accuracy is not good enough!**
- **Note zero point energies were an order of magnitude larger!**

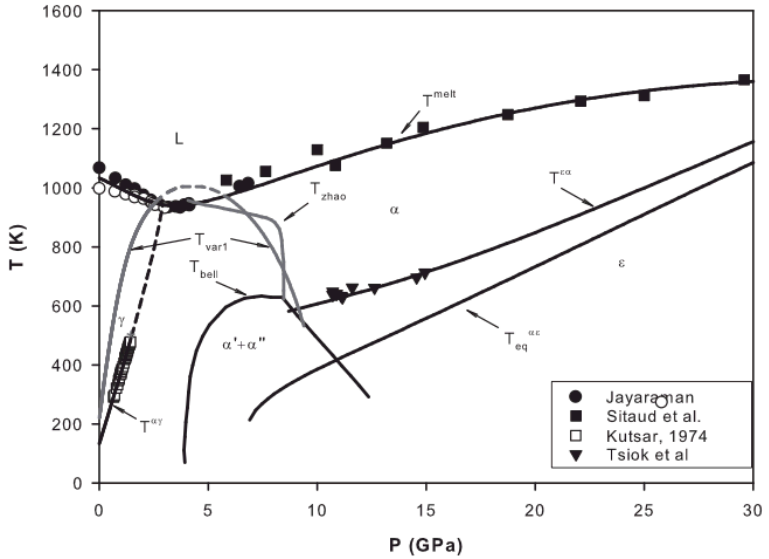




A wide variety of physics must be accurately calculated

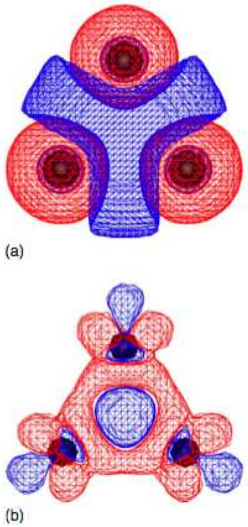
- **Van der Waals forces**
- **Localization vs delocalization**
- **Kondo physics**
- **Charge transfer**
- **Chemical Reactions**

Cerium Phase diagram



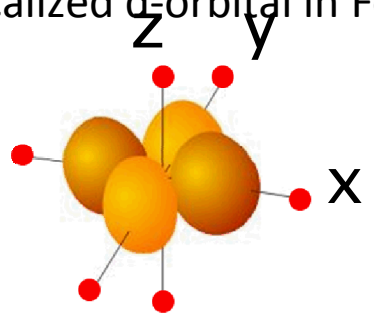
Elkin et al. PRB 84, 094120 (2011)

Xe isosurfaces



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

Localized d-orbital in FeO



e_g orbital with surrounding oxygen ions

Diffusion Monte Carlo solves many of these problems

- **Direct, stochastic solution of the many body Schrodinger equation**

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

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

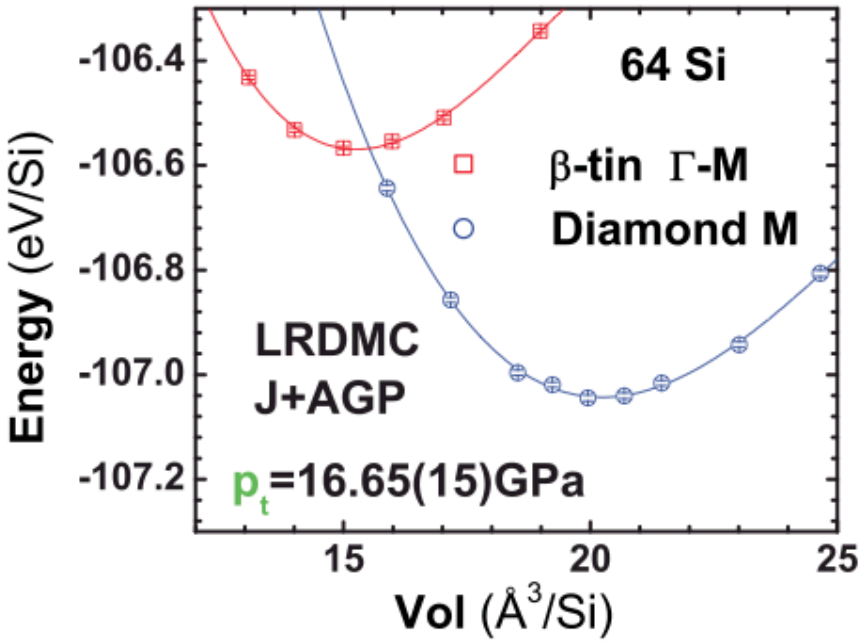
- **Must recast integrand as a probability distribution**
  - **Probability distributions must be positive everywhere**
  - **Wavefunction is not positive definite!**
  - **Restrict sampling using nodes of trial wavefunction**
- **Highly accurate calculations of the properties of condensed phases are possible**
  - **Electron Gas**
  - **Van Der Waals solids**
  - **Localized d-electrons**

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

Impact of approximations

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

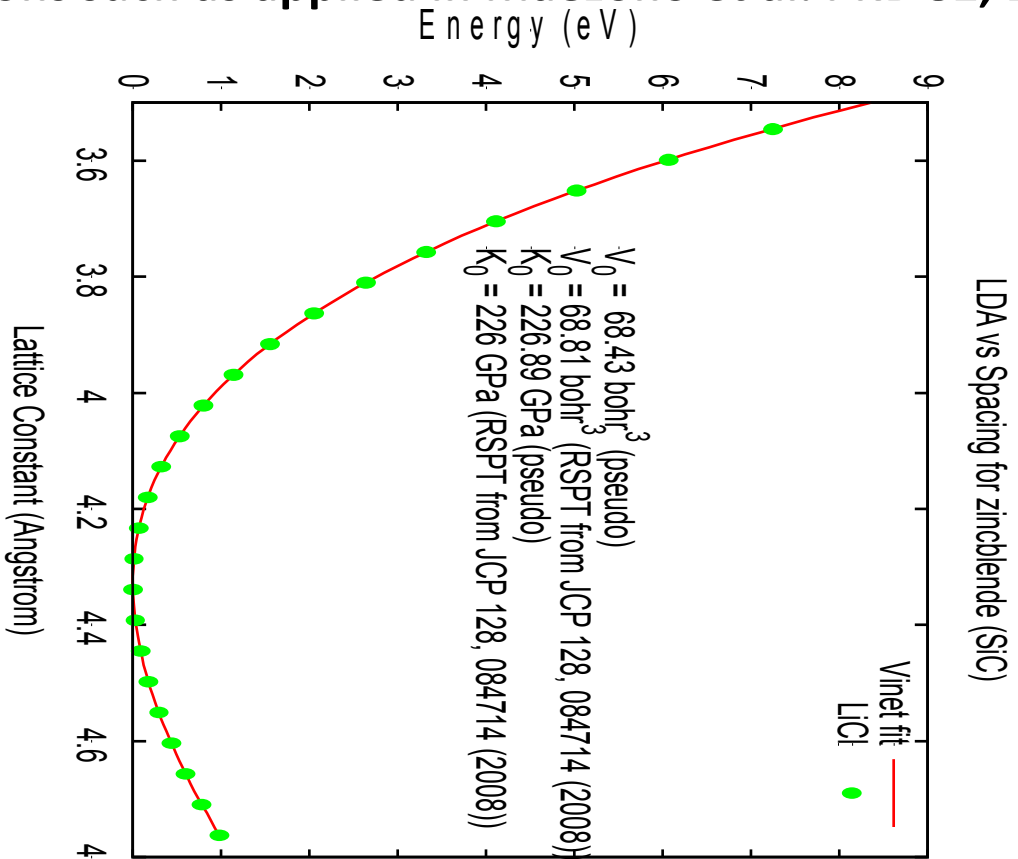


Method	Raw (GPa)	Corrected (GPa) (T = 300 K)
LDA	7.21	6.34
PBE	9.87	8.99
VMC	15.48 ± 0.06	13.3 ± 1.0
LRDMC	16.65 ± 0.15	14.5 ± 1.0
DMC (Ref. 18)	19.0 ± 0.5	16.5 ± 0.5
DMC (Ref. 13)	16.5 ± 1.0	14.0 ± 1.0
AFQMC (Ref. 20)	15.1 ± 0.3	12.6 ± 0.3
Expt.	10.0 – 12.5	10.0 – 12.5

Sorella et al. PRB 83, 075119 (2011)

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)



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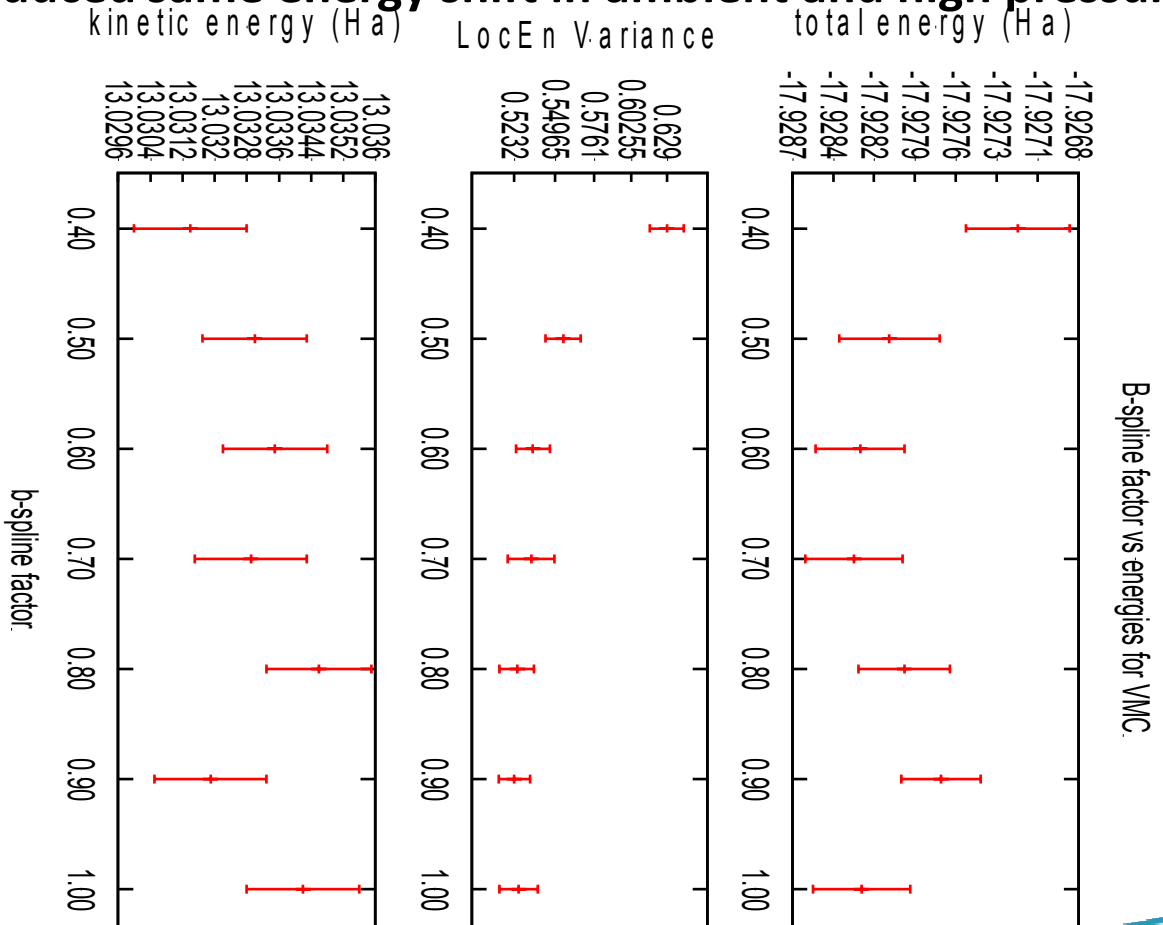
Convergence of technical parameters

- **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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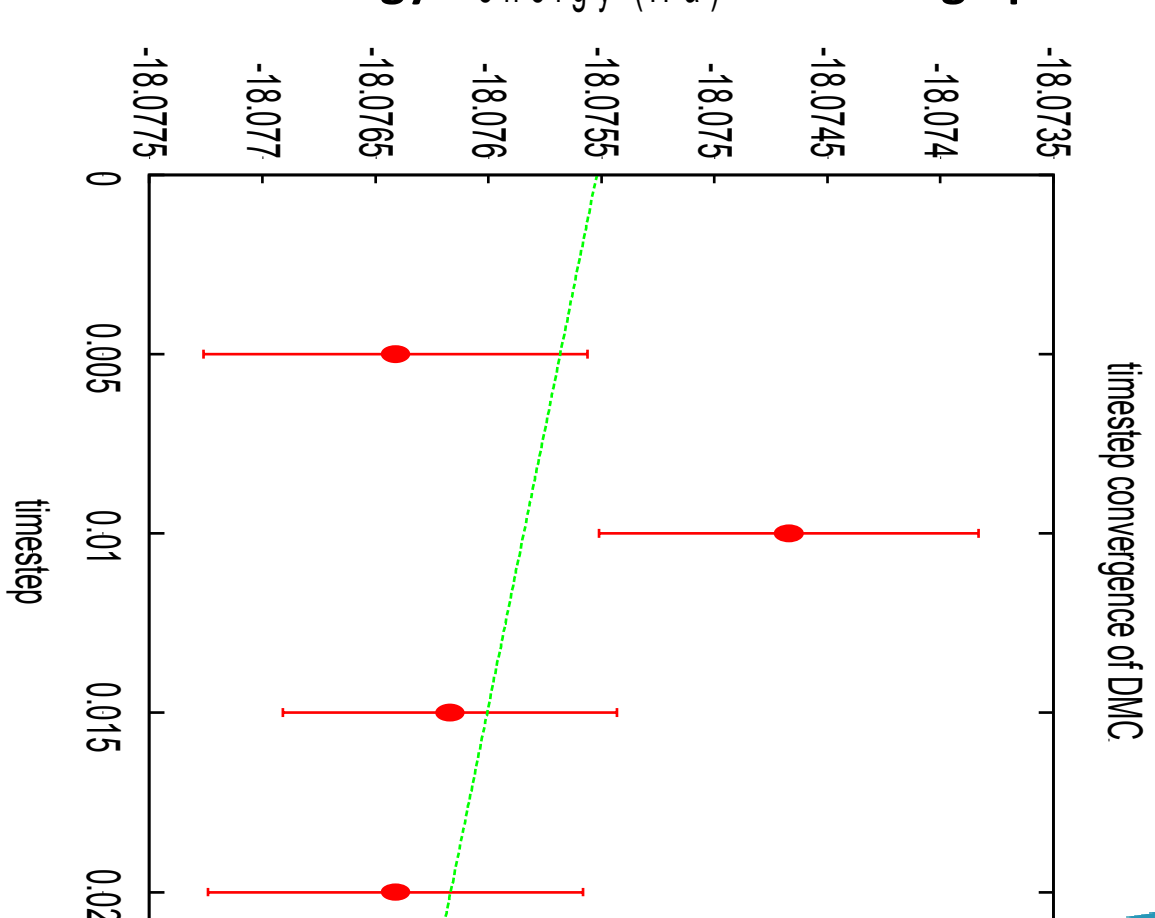

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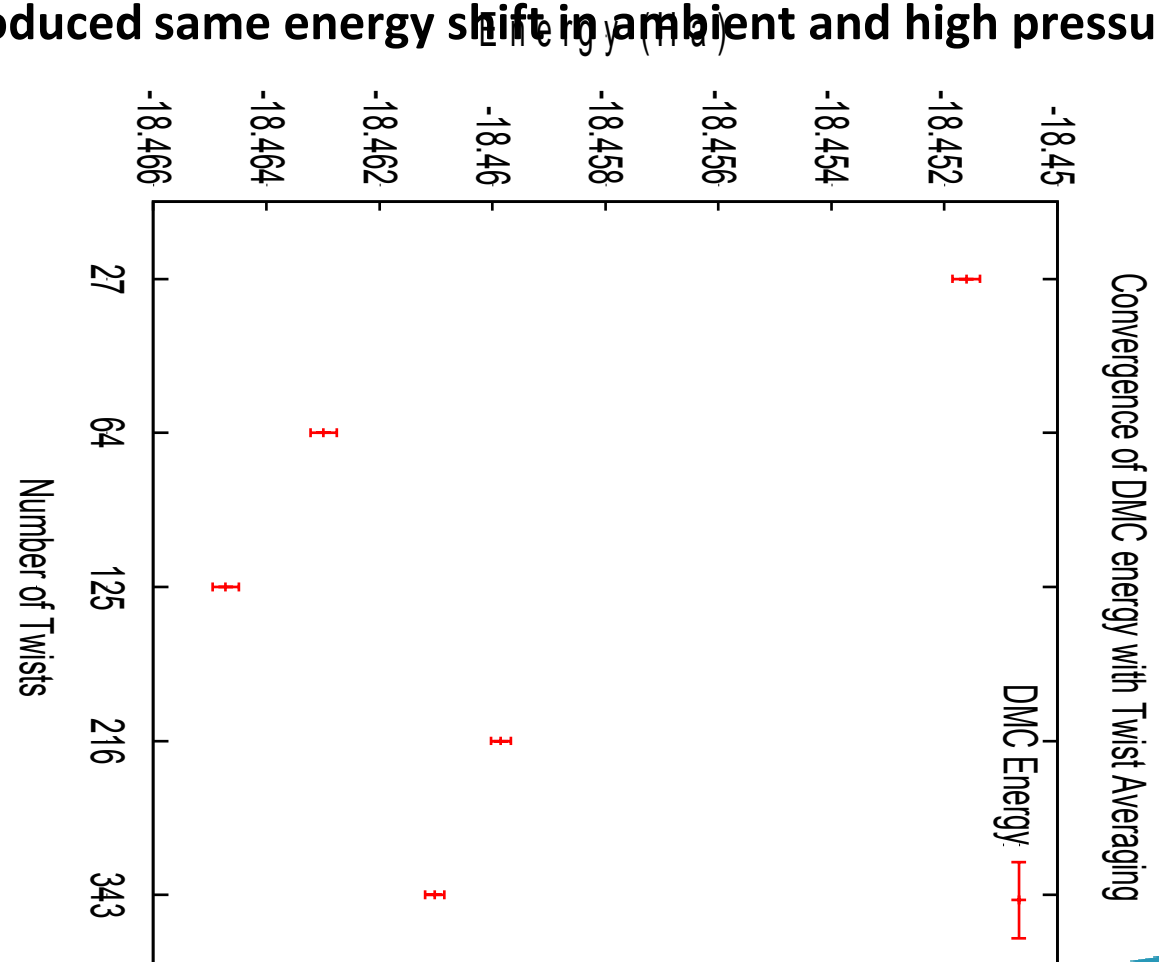

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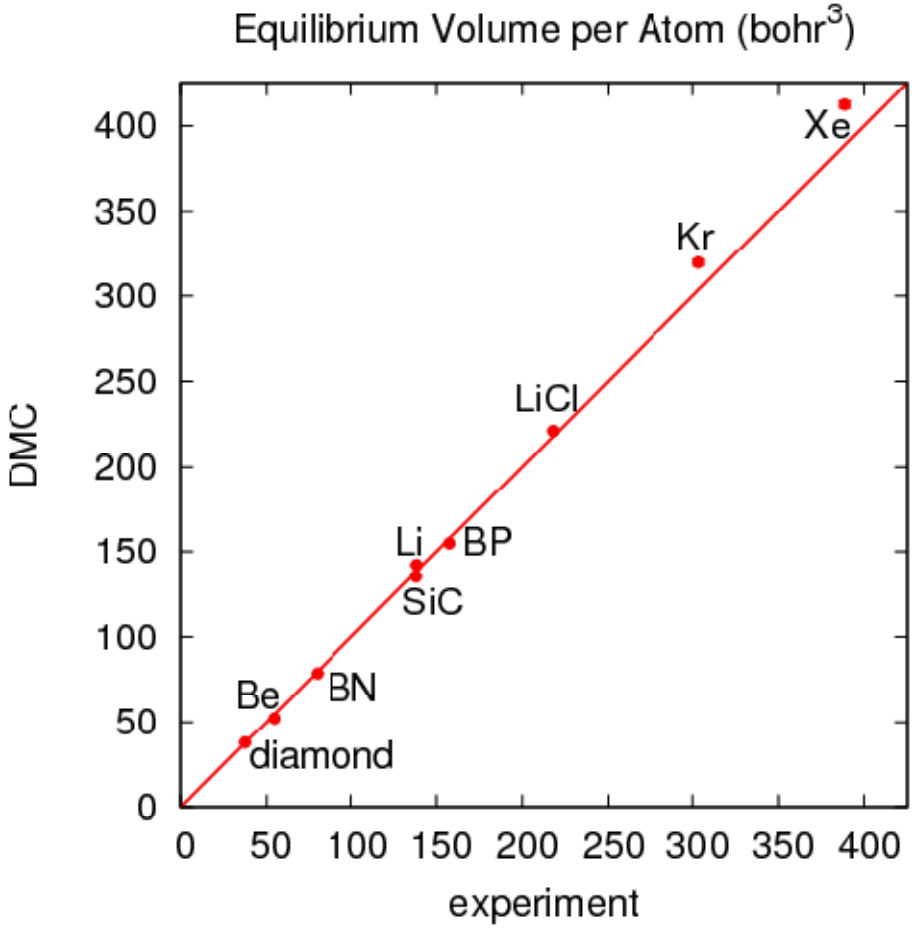
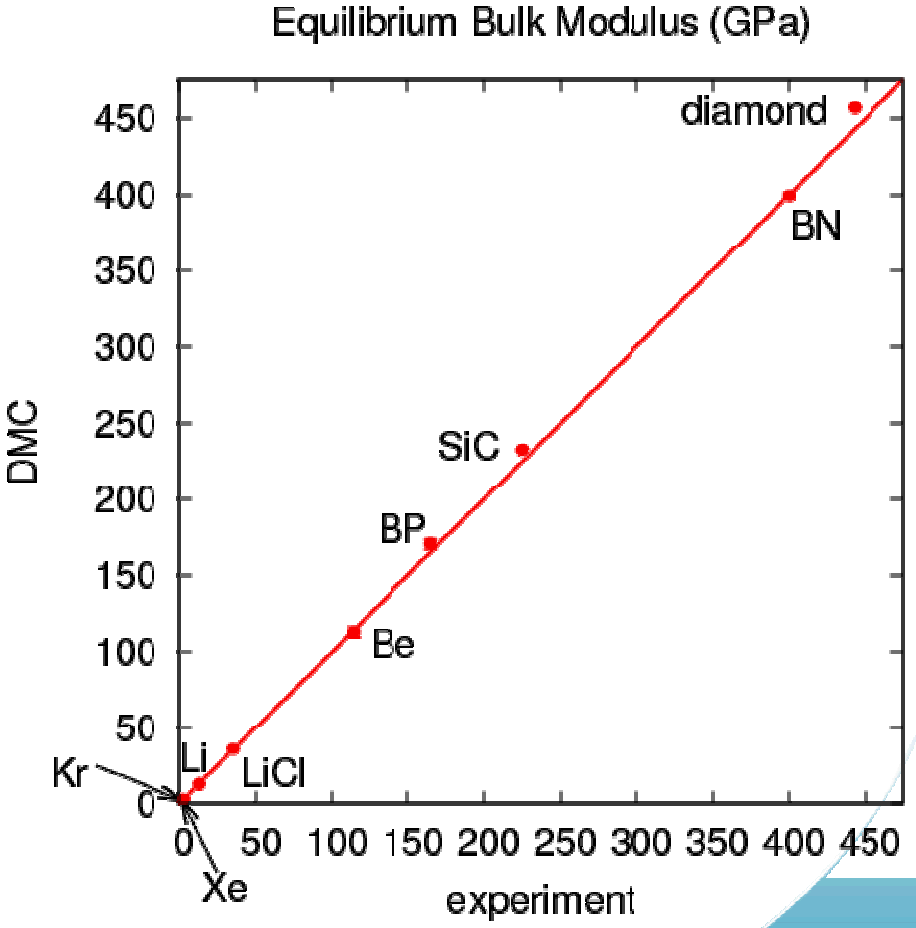
DMC results agree with experiment

- **Fit vinet form to E(V) and compare equilibrium lattice constant and bulk modulus to experiment**





QMC is a promising method for calculation of cold curves

- **Calculated equilibrium lattice constant and bulk modulus agree with experiment for a variety of materials**
- **A consistent approach was used for all calculations**
- **With specifically constructed pseudopotentials no correction from DFT is needed**
- **Difficulties were most pronounced for van der Waals compounds and the bulk modulus of diamond**