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# Applications of quantum Monte Carlo to materials at extreme conditions

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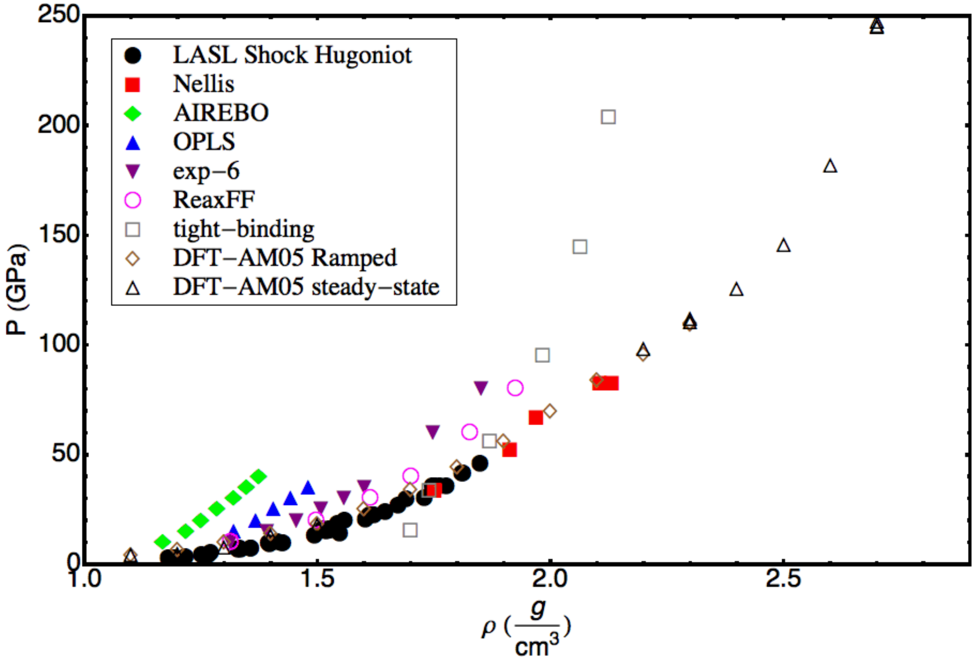
National
Laboratories

# Objectives

- **Provide an alternative to experiments which can be extremely expensive and difficult to perform**
- **Provide insight into mechanisms**
- **Achieve favorable computational scaling**
  - **Complexity**
  - **Parallel Efficiency**
- **Have no empirical or adjustable parameters → Predictive!!**



**“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

# Perhaps with Modern Computers?

- **For most materials ions are easy (classical)**
- **Electrons pose problem**
  - Schrödinger Equation $\hat{H}\Psi(r_1 \ldots r_N) = E\Psi(r_1 \ldots r_N)$

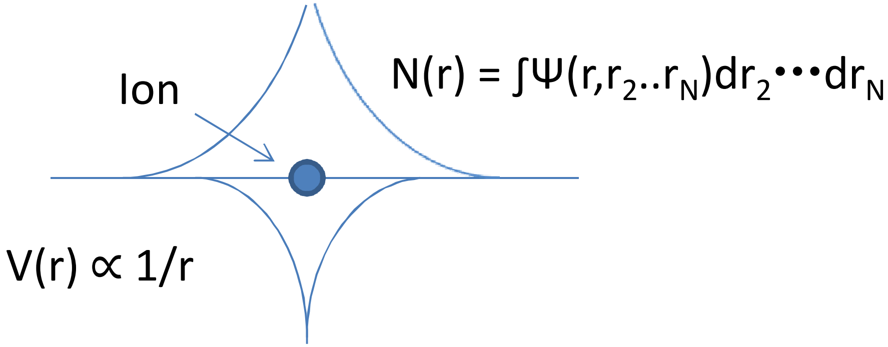
$$\hat{H} = -\sum_i \frac{\nabla_i^2}{2m} + \frac{1}{2}\sum_{i \neq j} \frac{e^2}{\left|\vec{r}_i - \vec{r}_j\right|} + \sum_{i,I} \frac{Z_I e^2}{\left|\vec{R}_I - \vec{r}_i\right|}$$

  - To solve naïvely on a grid
    - *3 dimensions per electron*
    - *20 points in each direction*
    - *$20^9$ ≈ 512 billion points for 3 electrons*

– 3.6 TB just to store!

# Physical Insight -> Density Functional Theory

- **Three insights make solving the quantum problem for the electrons tractable**
  - **Physical insight:**



$N(r) = \int \Psi(r, r_2..r_N) dr_2 \cdots dr_N$

    - *Wavefunction is not an observable but the density is*
    - *Replace the 3N dimensional wavefunction with density*
  - **Replace interacting electrons with noninteracting in an effective potential**
  - **Choose effective potential to be a local property of the density**

# Density Functional Theory (cont)

- **Remarkably successful at predicting properties**
  - Lattice constants
  - Binding energies
  - Phonon spectra
  - Etc. etc. etc.

- **Also has limitations**
  - Zoo of choices for exchange correlation functional
  - Locality (nature is nearsighted but not blind)
  - “strongly correlated” systems
- **Computational Efficiency**
  - Computationally expensive : 100-1000’s of atoms
  - Moderate Parallel Scaling

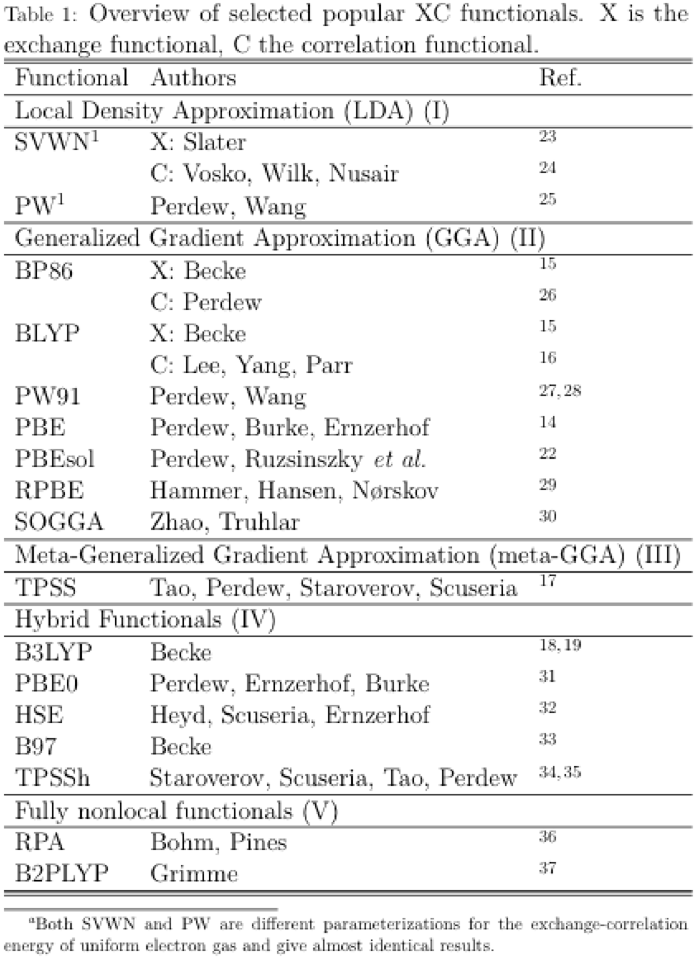


Table 1: Overview of selected popular XC functionals. X is the exchange functional, C the correlation functional.

| Functional | Authors | Ref. |
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| Fully nonlocal functionals (V) | | |
| RPA | Bohm, Pines | 36 |
| B2PLYP | Grimme | 37 |

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

# In search of a better method

- **Solve Schrodinger equation directly?**

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

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

- **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 ∝ $1/\sqrt{N}$

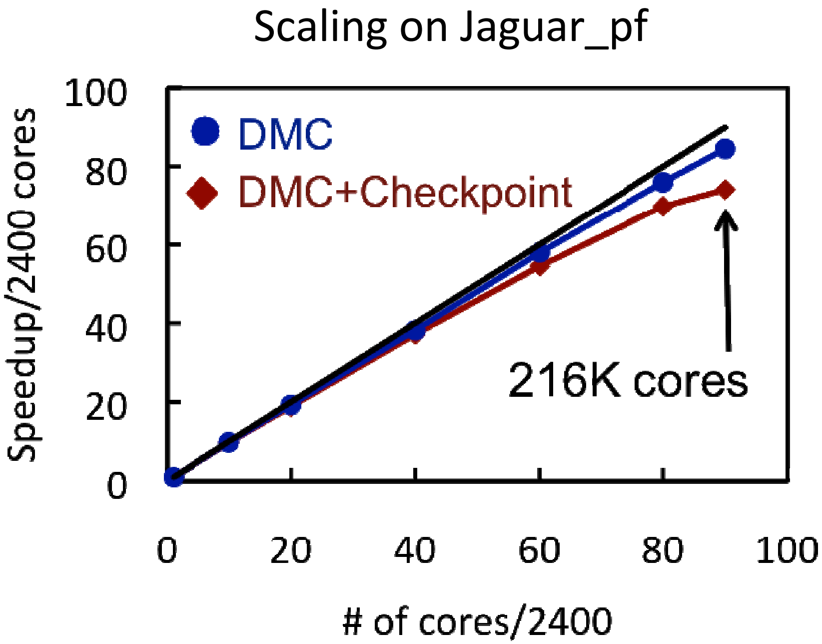
Circle area
~ 6/7 of square

# Stochastic Sampling + Schrodinger Equation = Quantum Monte Carlo

- **Integral still exists in a very large space**
  - Guide sampling according to trial wavefunction from another method
  - 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)

# QMCPACK – Massively Parallel QMC

- **Quantum Monte Carlo code designed for massive parallelism**
- **Developed by J. Kim et al at the University of Illinois Urbana-Champaign**
- **Hybrid MPI / OpenMP parallelism**
  - **Shared Memory on Nodes, Distributed between**
- **Can efficiently scale to more than 100,000 CPU cores**



# Massive Parallelism: Blessing and Curse

- 2-3 orders of magnitude more effort required than DFT
- How to get enough FLOPs?
- Note similarities to computer graphics

- In 3D graphics images are made of many polygons
- Movements require multiplying matrices by a vector of points for each polygon
- Massively parallel

# Specialized Hardware – the GPU

- Graphics cards have acquired immense power for this task
- NVIDIA GF100 GPU
  - 512 Processor cores
  - 1.4 Ghz clock frequency
  - 177 GB/s Memory Bandwidth
- Problem is getting enough data to processors
- Hide Latency with pipelining and threads

```
If (A>4) then
   B = A+C
Else
   B = A+D
Endif
```

| Clock Cycle | Operation |
|---|---|
| 1 | Load A |
| 2 | Load C |
| 3 | Check A > 4 |
| 4 | B = A+C |

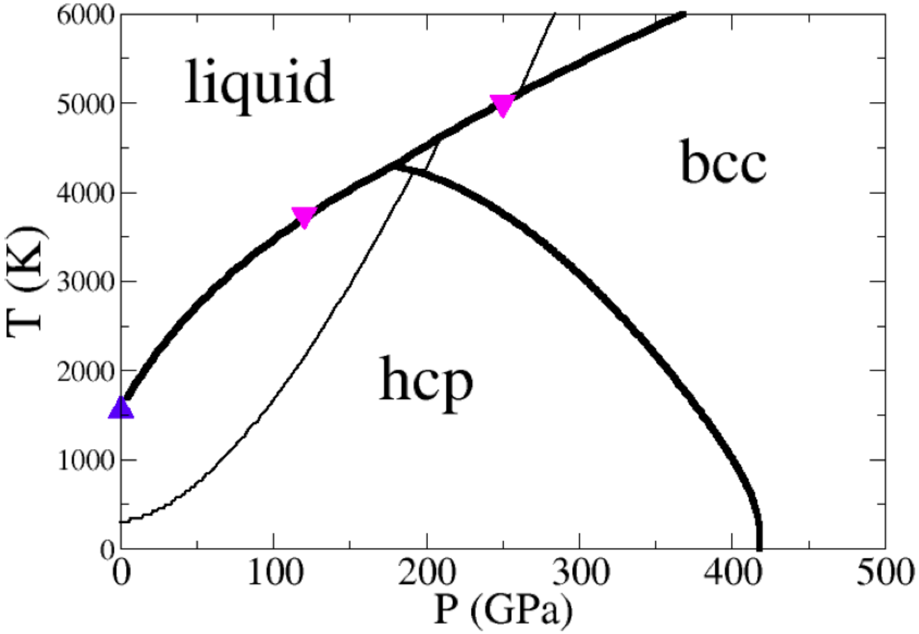
| Clock Cycle | Operation |
|---|---|
| 1 | Load  Thread 1 A |
| 2 | Load Thread 2 A |
| 3 | Load Thread 3 A |
| 4 | Check Thread 1 A > 4 |

# Applications

- **Solid-Solid phase transformations in Be**
- Melting of Xe under pressure
- Magnetic properties of FeO
- Choosing Functionals for QMD calculations

# Accurate properties of solid Be from QMC

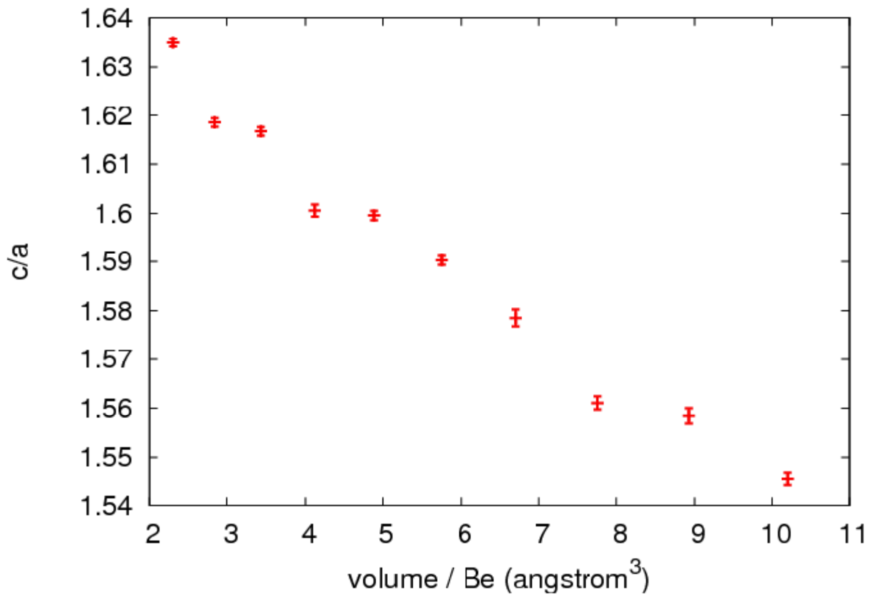
- Solid Be used in ICF
  - High strength, low Z material, Low x-ray absorption
- Light element poses no obvious theoretical problems
- HCP at ambient temperature and pressure
- Phase transition to BCC at high pressure
- Prototype for future studies



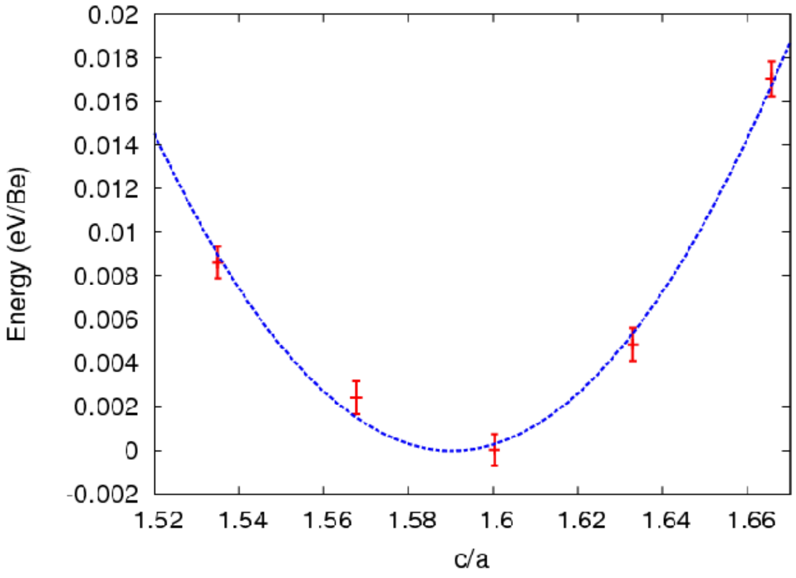
# Importance of geometry: pressure dependence of c/a

- **Be has unusually small c/a at ambient pressure**
  - c/a approaches ideal value at high pressures
- **Forces are not available so geometry optimization is manual**

Optimal strain vs volume

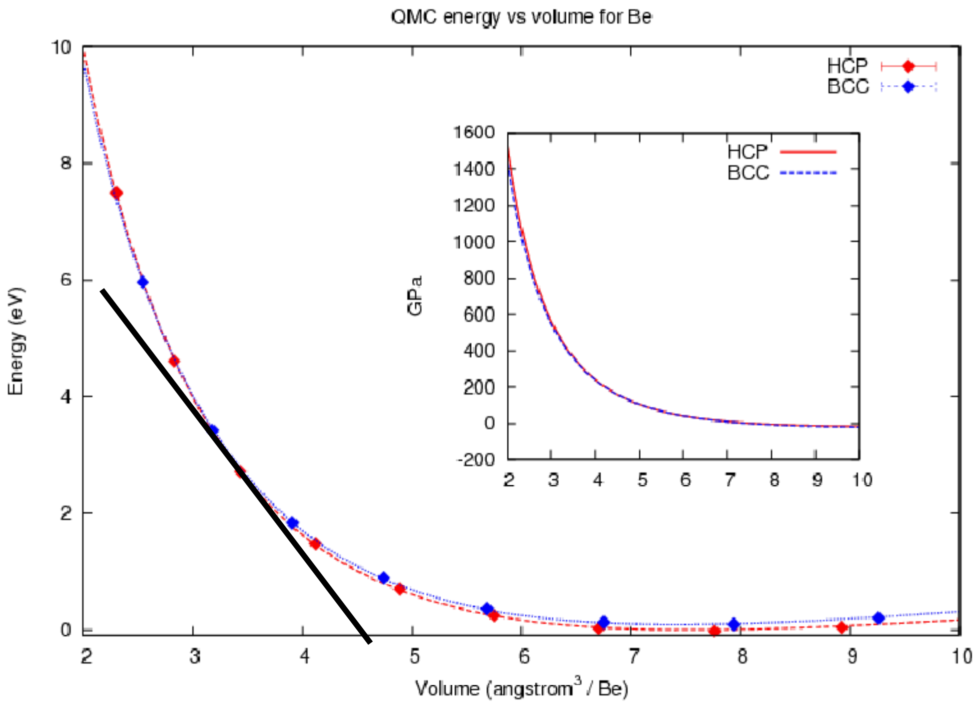


Strain vs Energy at 3.8 bohr



# Phase transition at much higher pressure than previously thought

- **Equation of state is fit using Vinet form**
  - More crucial because values have statistical errors
- **Phase transition occurs at > 700 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) | 7.796 +/- 0.008 | 8.014 |
| Bulk Modulus (Gpa) | 114 +/- 2 | 116.8 |

# Applications

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- Magnetic properties of FeO
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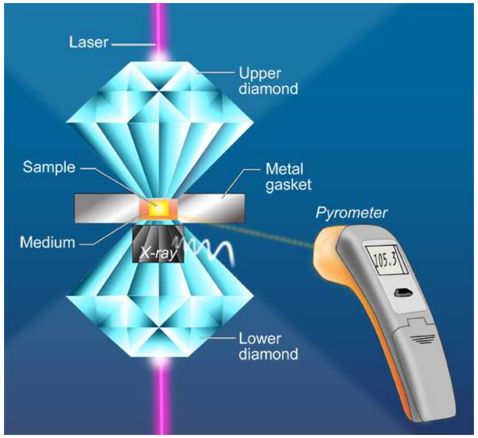
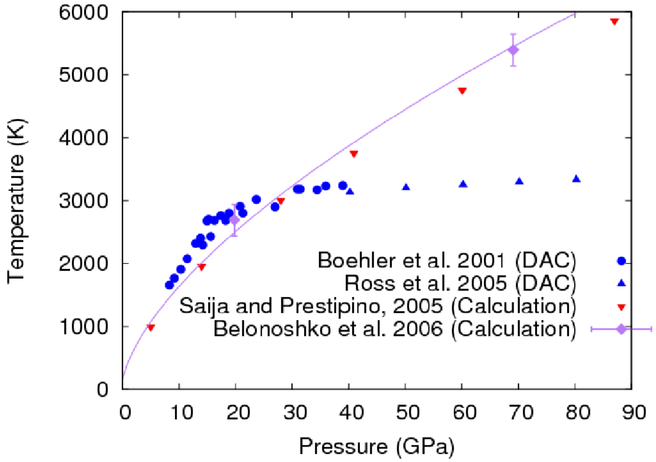
# Xe melting: disagreement between DAC and DFT

- **Disagreement between melting under pressure between DAC, ab initio calculations and shock measurements is common**
  - See for example  Ta, Fe, MgO and Xe
- **Many sources of uncertainty**
  - DAC
    - *Anisotropic Stress, Reactivity, Ambiguous Phase Assignment*
  - Shock
    - *Temperature measurements*
  - Ab Initio
    - *DFT Approximations, convergence*
- **Xe : Demanding for ab initio**
  - Van der Waals effects in DFT
  - But the Hugoniot was calculated and measured with great accuracy and agreement
    - *Root et al. PRL **105**, 085501 (2010)*
    - *Constrained EOS at high temperatures and pressures*

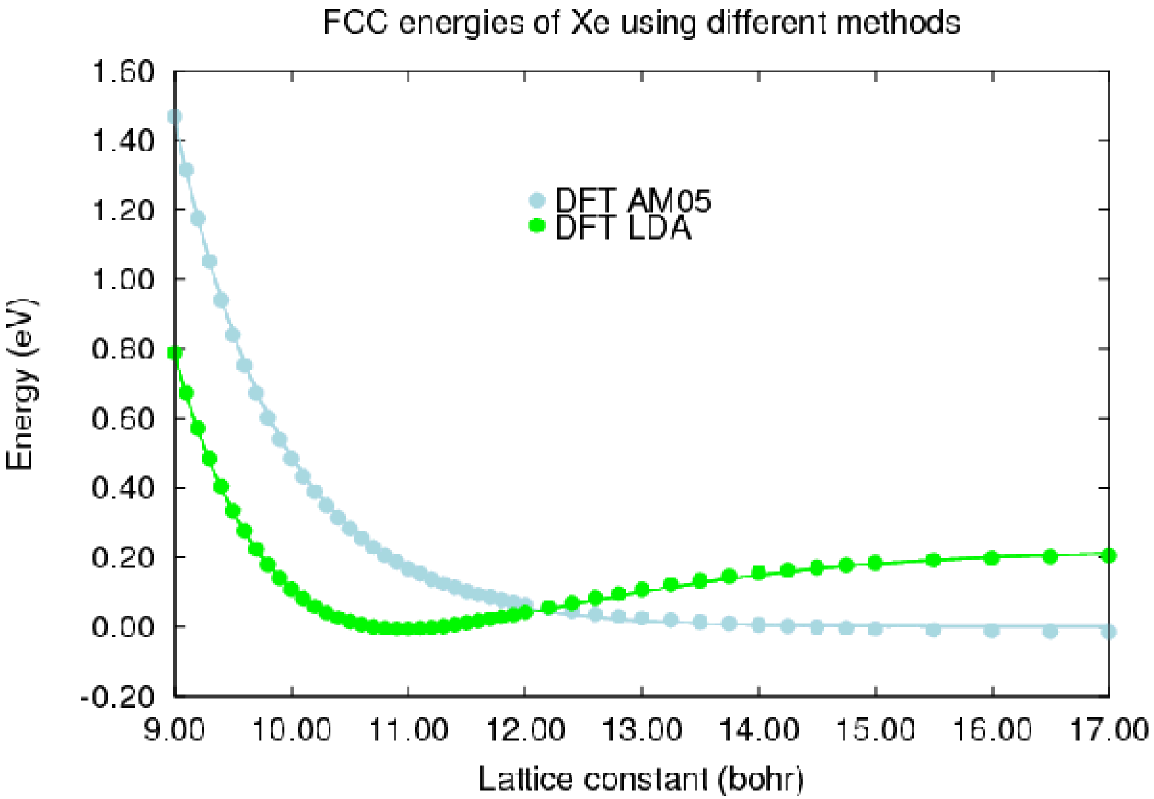


Klug, Physics. **3**, 52 (2010)



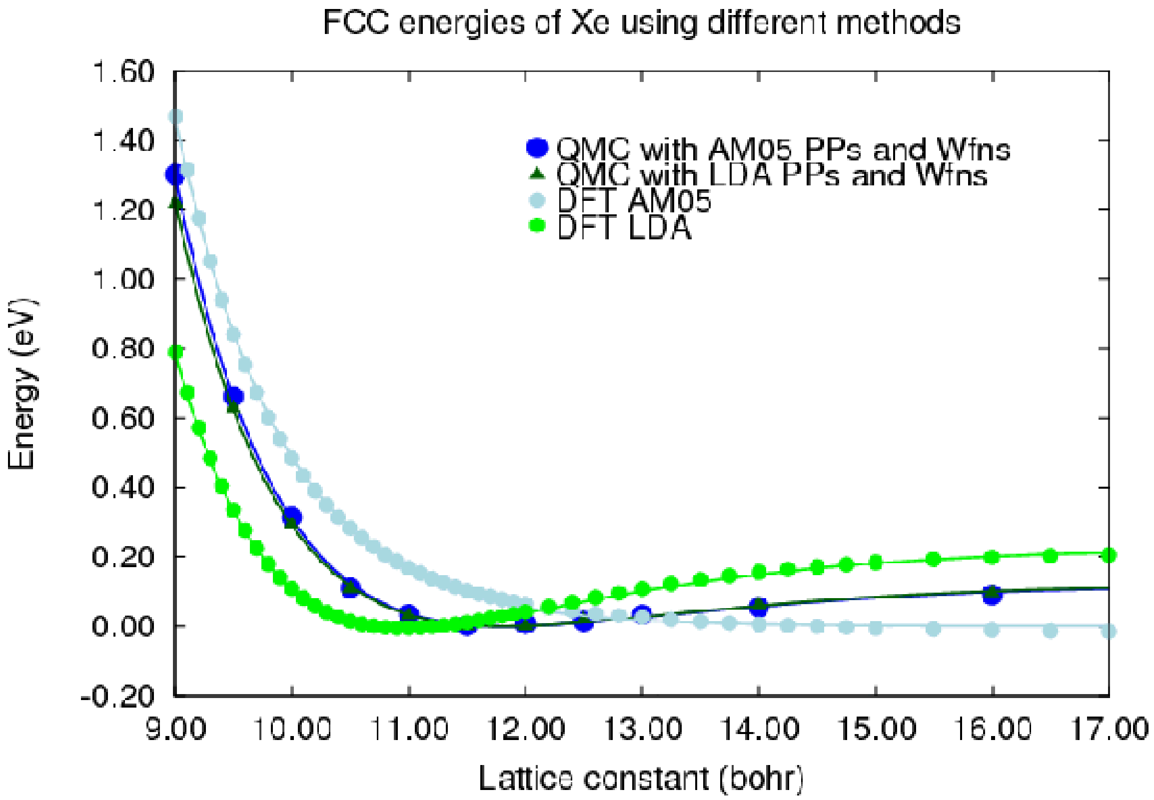
# Fixed node approximation and DFT Functional

- **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



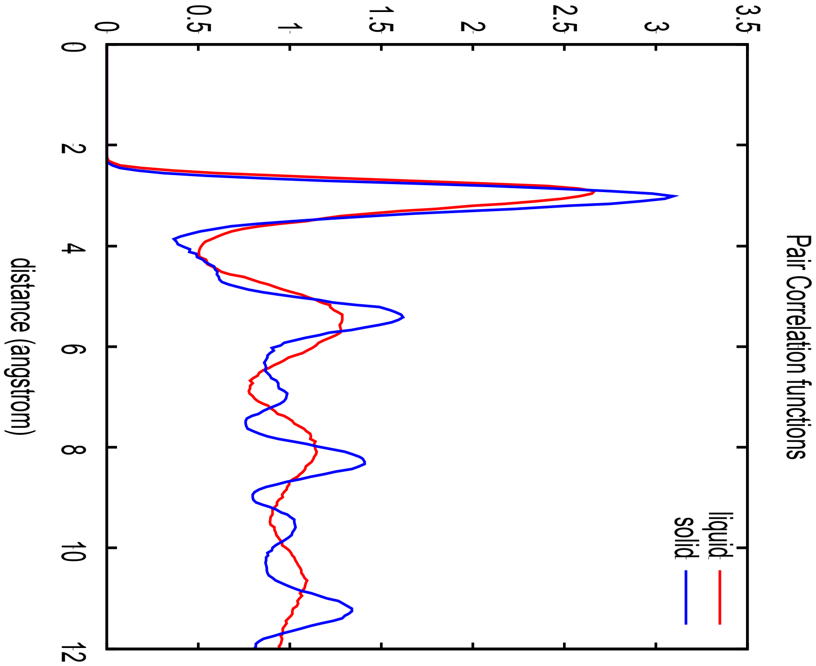
# Fixed node approximation and DFT Functional

- **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
  - DMC with nodes and pseudopotentials taken from above calculations
    - *Very small dependence on DFT trial wavefunction*



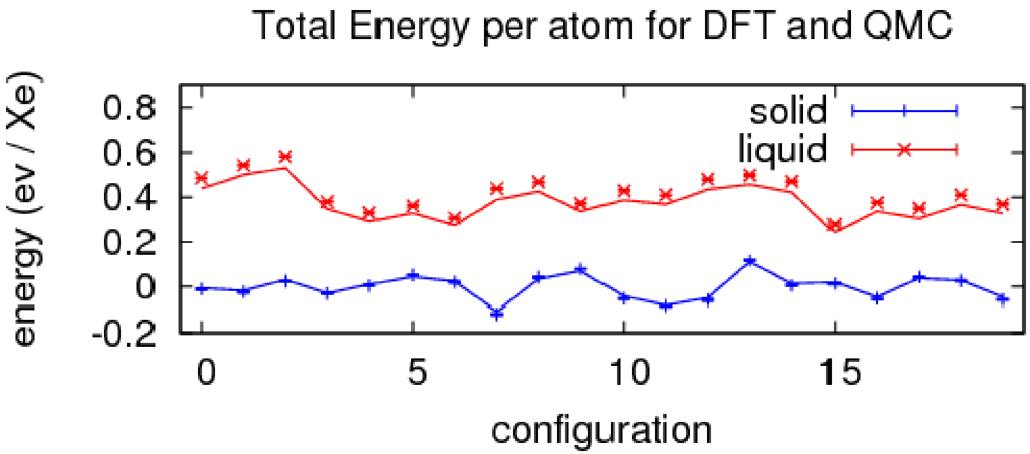
# Sample high temperature phase space with DFT

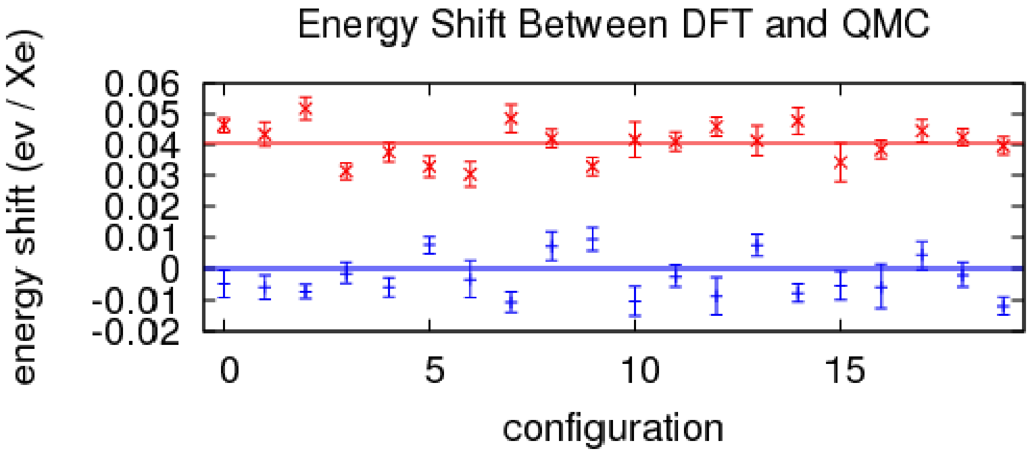
- **Quantum MD calculations performed with VASP using the LDA functional**
  - **Leverage two phase melt calculations by Belonoshko et al.,** PRB **2006**
- **Trial wavefunctions produced using quantum espresso**
- **108 atom simulation cells to minimize finite size effects**
- **Ramp temperature starting from a solid and a liquid**
- **Perform long metastable simulations at phase coexistence point**
- **Monitor Pair Correlation function**



# DMC calculations of solid and liquid snapshots

- **20 snapshots from 108 atom solid and liquid LDA runs at 6000 K**
- **Fluctuations of QMC energy about LDA energies are small**
- **Energy difference between liquid and solid 0.0406 +/- 0.0027 eV / Xe greater in DMC**


Total Energy per atom for DFT and QMC


Energy Shift Between DFT and QMC

# Thermodynamic Integration approach to melting: using QMC to refine DFT

- Use thermodynamic integration to calculate relative change in Helmholtz free energy going from DFT to QMC

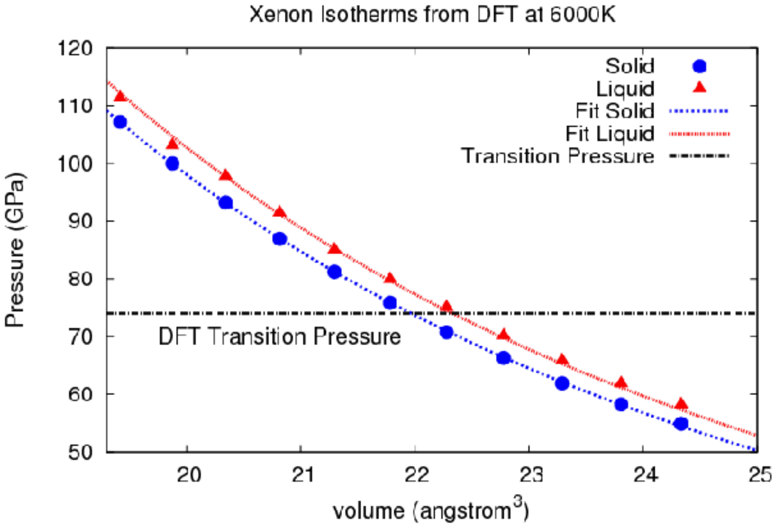
$$\Delta F = \int_0^1 d\lambda \langle \Delta U \rangle_\lambda \approx \langle \Delta U \rangle_{\lambda=0} - \frac{1}{2k_B T} \left\langle (\Delta U - \langle \Delta U \rangle_{\lambda=0})^2 \right\rangle_{\lambda=0}$$

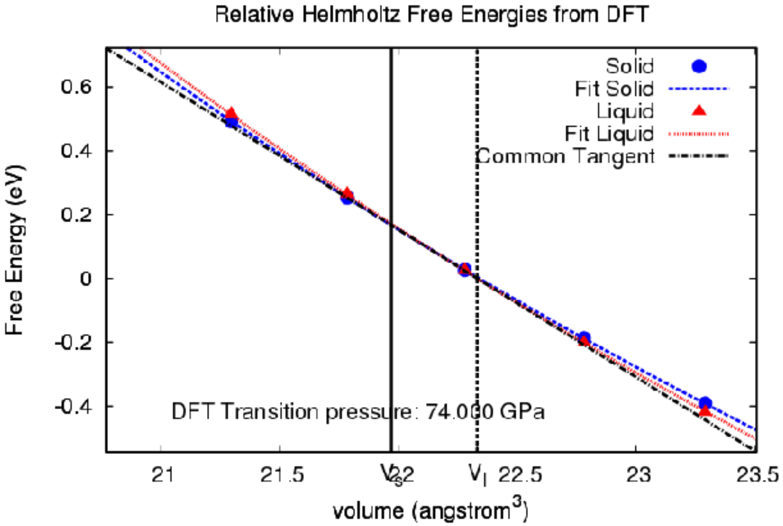
- The change in melting temperature between DFT and DMC is

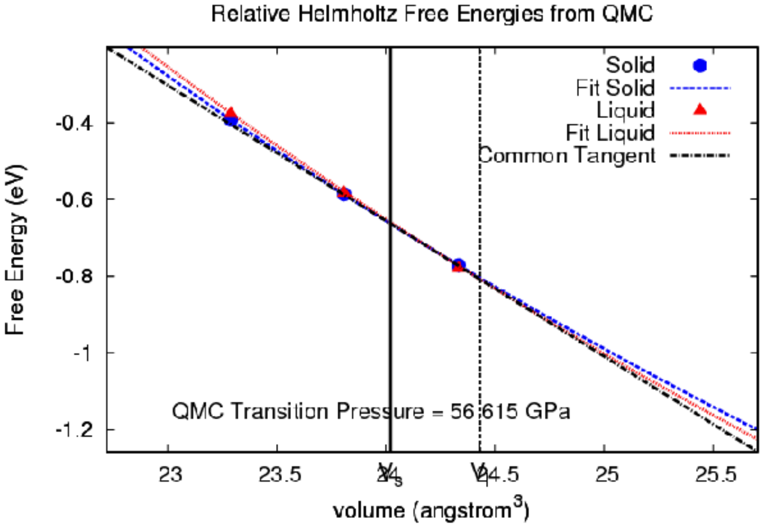
$$\Delta T_m \approx \frac{\Delta G^{ls}}{S_{DFT}^{ls}} \qquad \Delta G \approx \Delta F - V\Delta p^2 / 2K_T$$

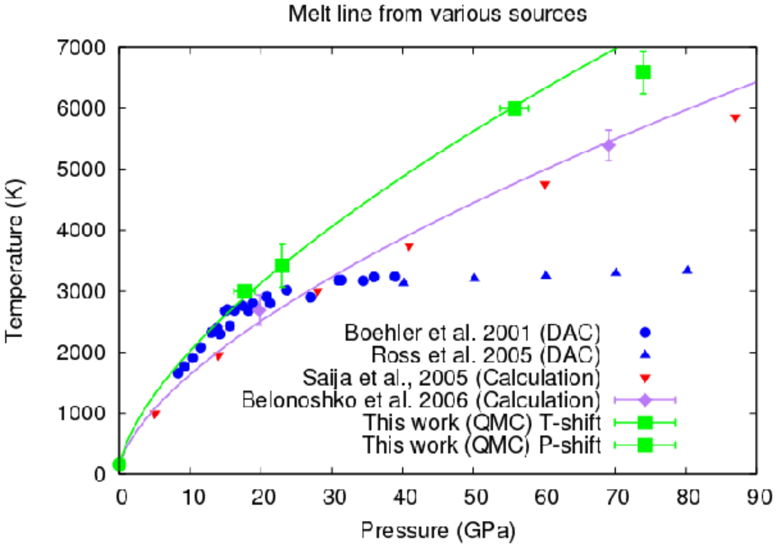
- Assume that difference in dynamics between DFT and DMC is small (fluctuation terms above are small)
- Can also use shift in Helmholtz free energy to get temperature shift at constant temperature

# Use Thermodynamic Integration to shift Melt Curve


Xenon Isotherms from DFT at 6000K

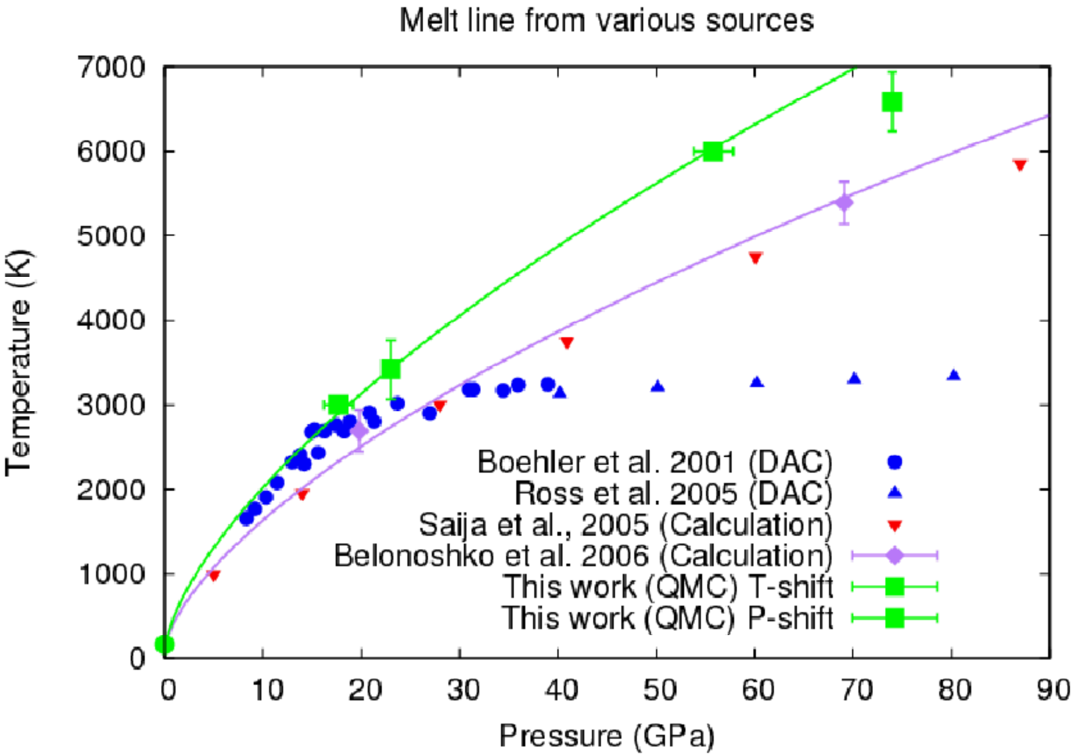

Relative Helmholtz Free Energies from DFT


Relative Helmholtz Free Energies from QMC


Melt line from various sources

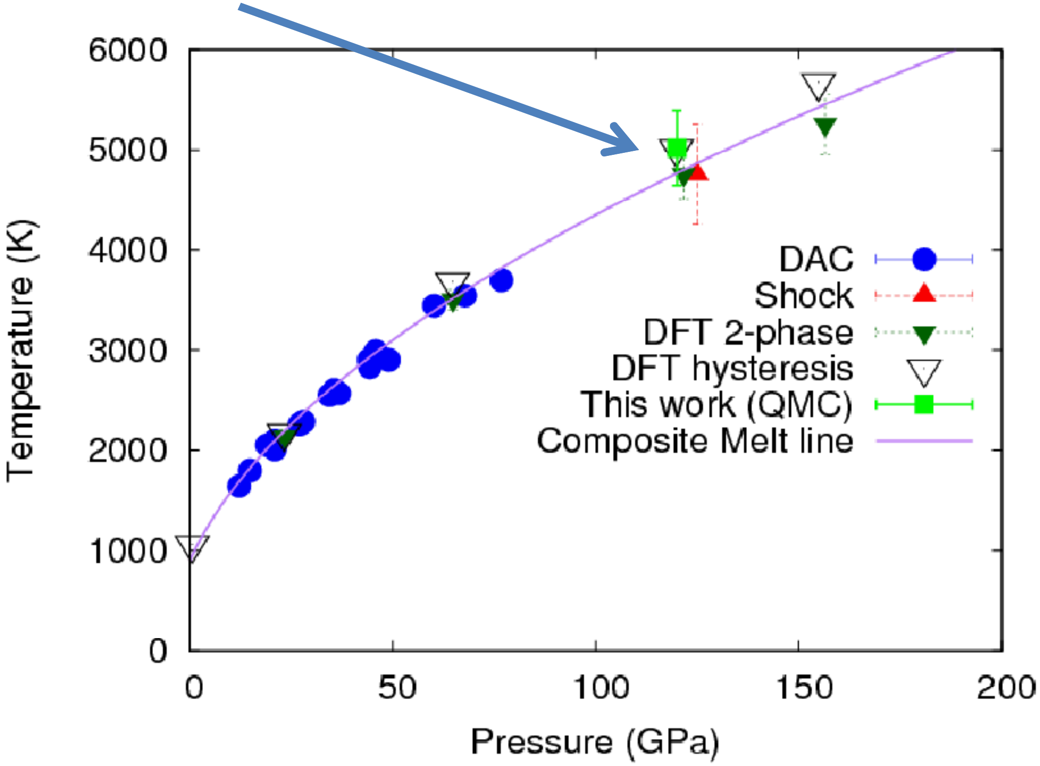
# QMC revised melt curve for Xe:

- **We found that diffusion Monte Carlo can accurately treat Xe under pressure**
- **Relative energies from DFT/LDA are accurate compared to DMC near 1 Mbar**
- **Errors in total energies from DFT/LDA will increase melting temperature**
- **Simon melt curve fit to two QMC points and ambient experimental data**
  - Agrees with DAC at low pressure
  - Conflicts at high pressures



# Validation of Method: Melting of Aluminum

- Magnitude of Xe melt curve correction similar to Sola and Alfe. PRL 130, 078501 (2009)
- Shock and DAC melt agree at high pressure
- DFT (2 phase approximation) accurately reproduces melt curve
- Thermodynamic integration from DFT to QMC gives a shift of only 18 K !

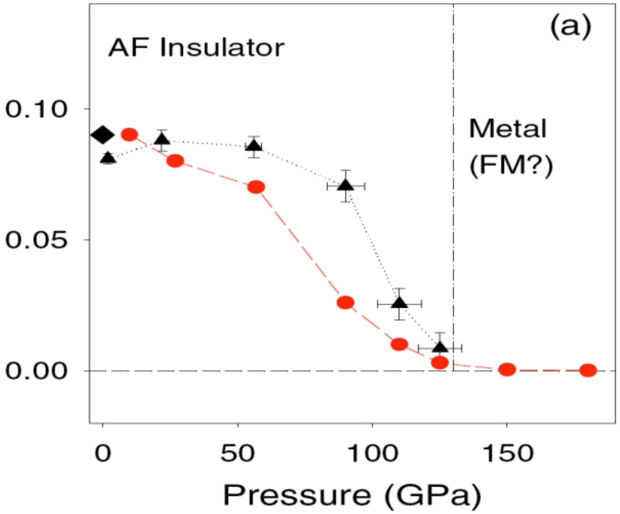


# Applications

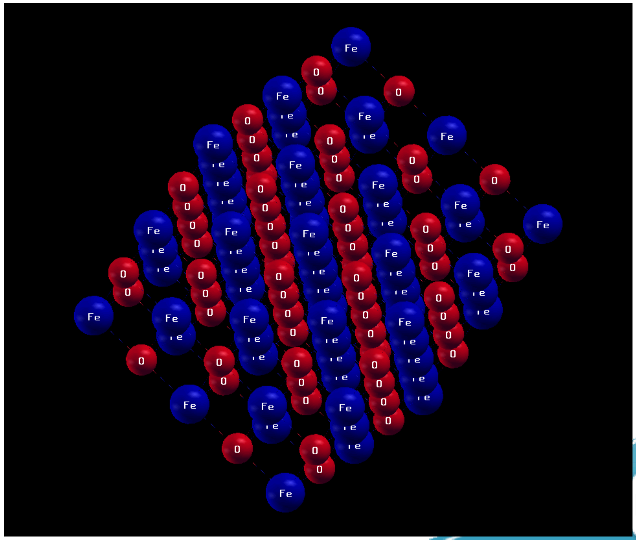
- Solid-Solid phase transformations in Be
- Melting of Xe under pressure
- **Magnetic properties of FeO**
- Choosing Functionals for QMD calculations

# Background: FeO

- **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**
- **Difficult to make stoichiometric FeO in the lab (vacancies yield $Fe_{1-x}O$ where x ~ 0.07)**
- **Rich electronic structure under pressure with a moment collapse and metallization**



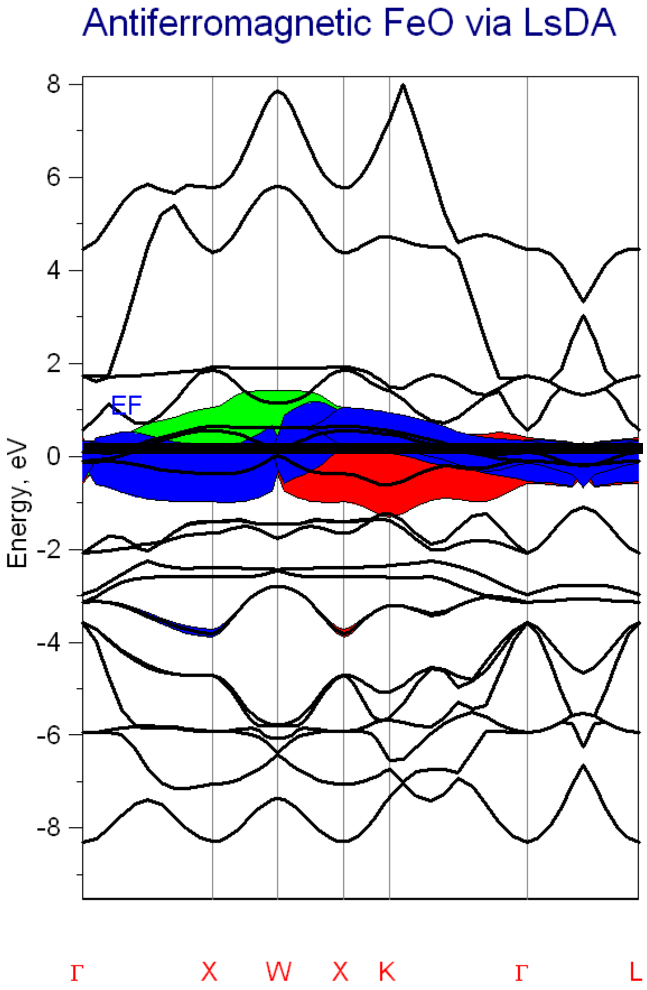
Experimental activation energy for conduction under Pressure from V. V. Struzhkin *et al.*, Mater. Res. Soc. Symp. Proc. **987**, 0987 (2007)



# DFT Applied to FeO : measured success

- **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



# LDA+U Applied to FeO : Fixing the mean field?

- **Introduce parallel system of localized electrons**
- **Hamiltonian split**

$$E^U[n,\{f^\sigma\}] = E^{LDA}[n] + E^U[\{f^\sigma\}] - E^{dc}[\{f^\sigma\}]$$

- **LDA+U recovers the insulating character**
- **Results are strongly dependent on model parameters: U and J**

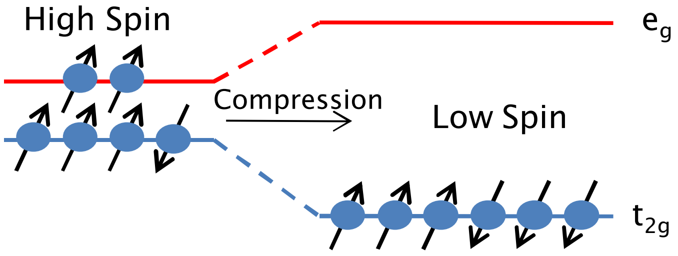
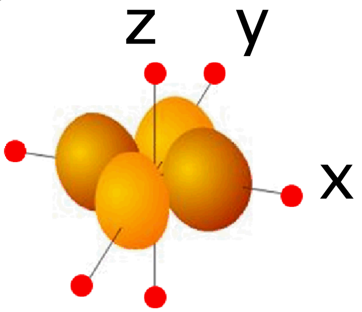
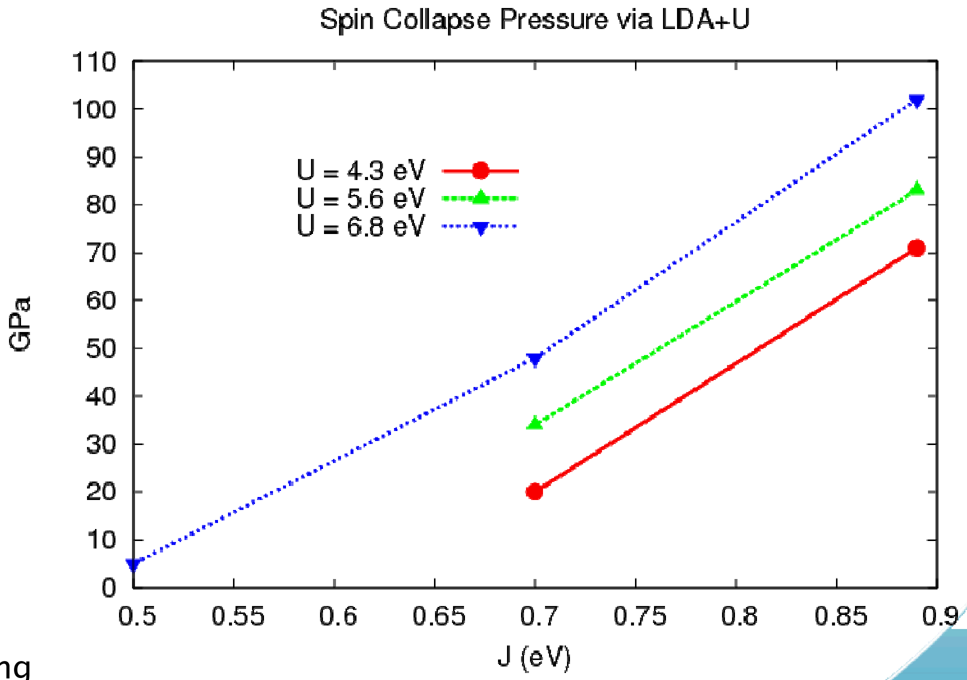


Figure adapted from :
Kunes et al. Nature Materials 7, 198 (2008)

- High Spin Energy
  $U+10J+2\Delta_{CF}$
- Low Spin Energy
  $3U+6J$



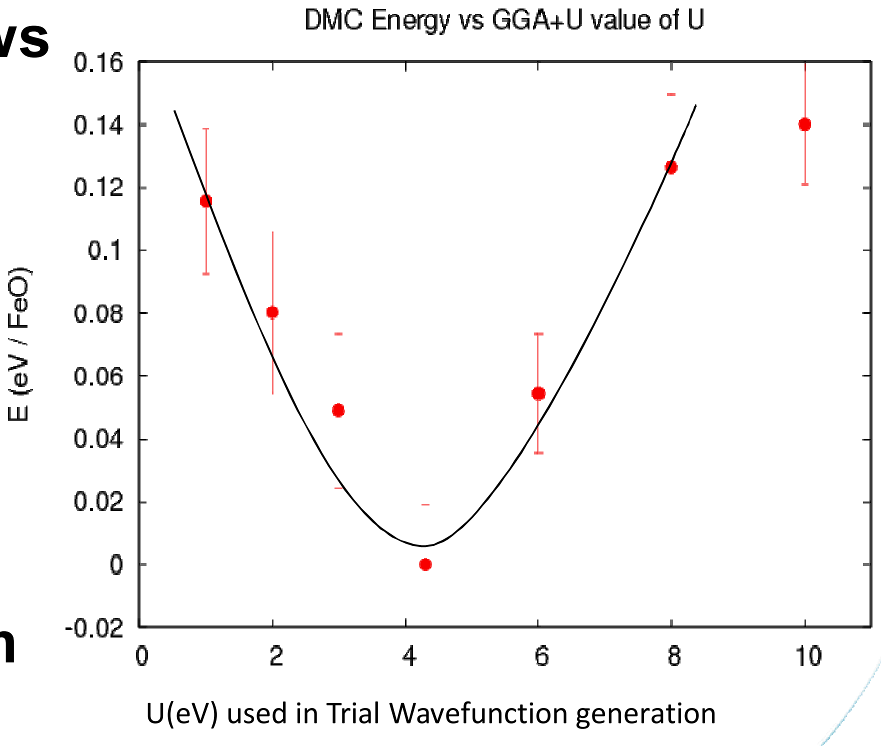
$e_g$ orbital with surrounding oxygen ions



Results generated with LMTART,
Full potential LMTO calculations

# Evaluating Wavefunctions: Choosing U with QMC

- **QMC is variational, so wavefunctions with different U can be compared on equal footing**
- **Variational Monte Carlo shows different energy profile than Diffusion Monte Carlo**
- **Shallow minimum at U=4.3 eV**
- **Minimum not strongly dependent on magnetic state or volume**
- **Does not necessarily confirm LDA+U approach**



# No Ferromagnetic State Found for FeO

- 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 |

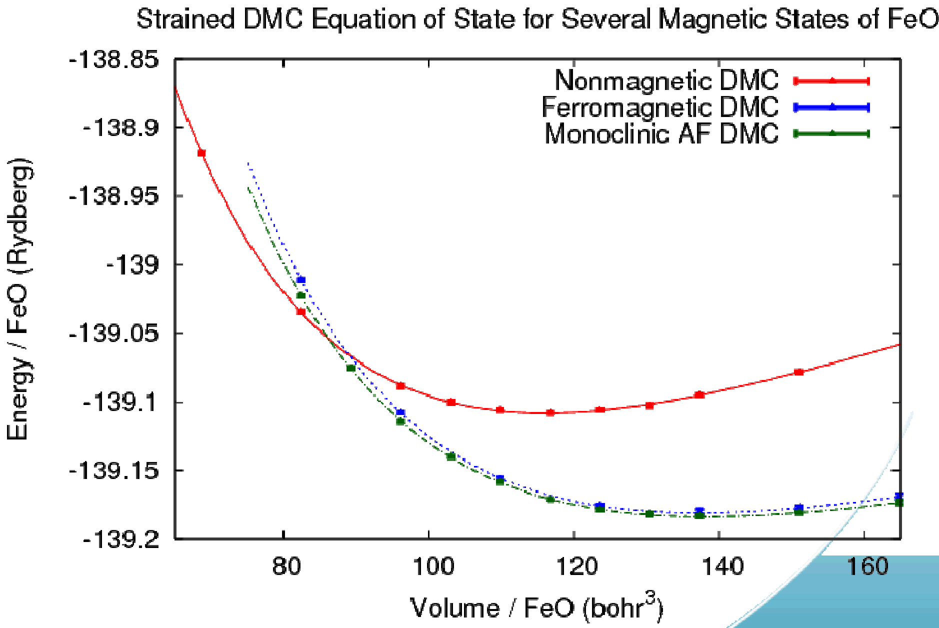


Chart adapted from Kolorenc et al. PRL 101, 185502 (2008)
Lattice Const from Hjortsberg et al. PRB 37, 3196 (1988)
Derivative quantities from McCammon et al., Phys Chem Miner 10, 106 (1984)

# Applications

- Solid-Solid phase transformations in Be
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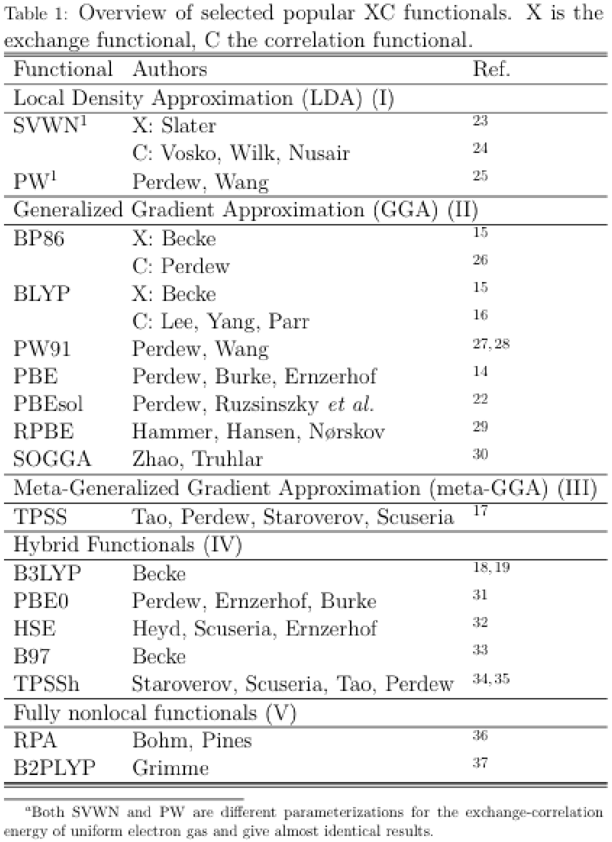
- **Choosing Functionals for QMD calculations**

# QMC can be used to choose between DFT functionals

- **QMC is not yet practical for MD simulations**
- **There is no a priori way to choose the functional for a DFT calculation**
  - Moving higher levels of approximation does not guarantee higher accuracy
- **Can choose to reproduce experimental values**
  - Lose predictive capability
  - Experimental data is not always available or reliable
- **Can choose functional that best reproduces results from a more accurate method**



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| B2PLYP | Grimme | 37 |

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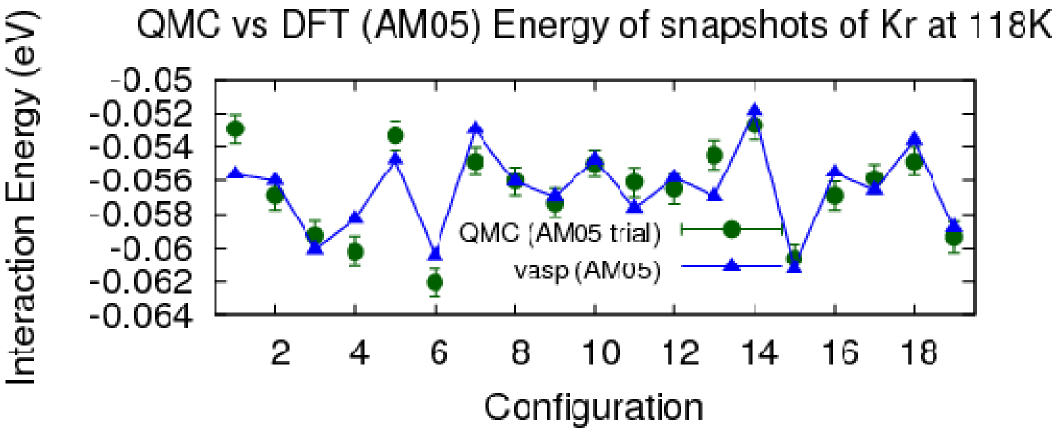
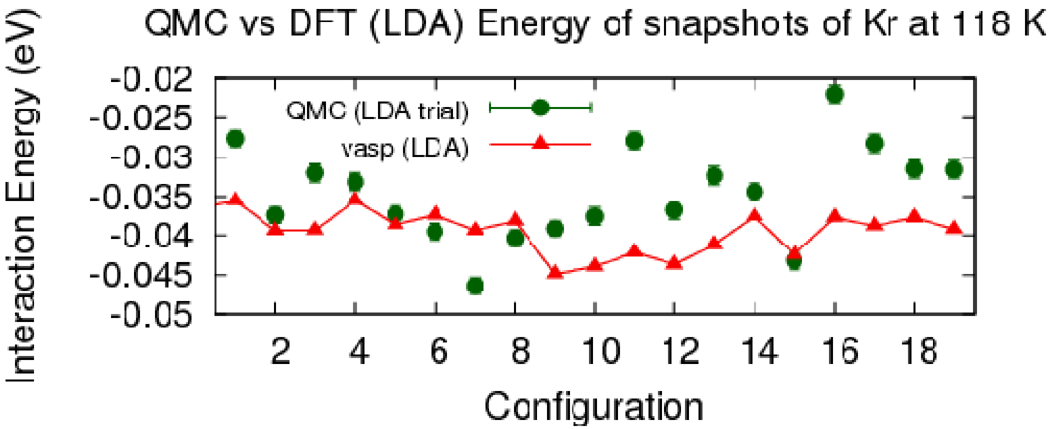
[a] Both SVWN and PW are different parameterizations for the exchange-correlation energy of uniform electron gas and give almost identical results.

D. Rappoport et al. in Encyclopedia of Inorganic Chemistry. R.B.King et al eds. Wiley (2009)

# LDA a poor choice for initial condition of Kr Hugoniot

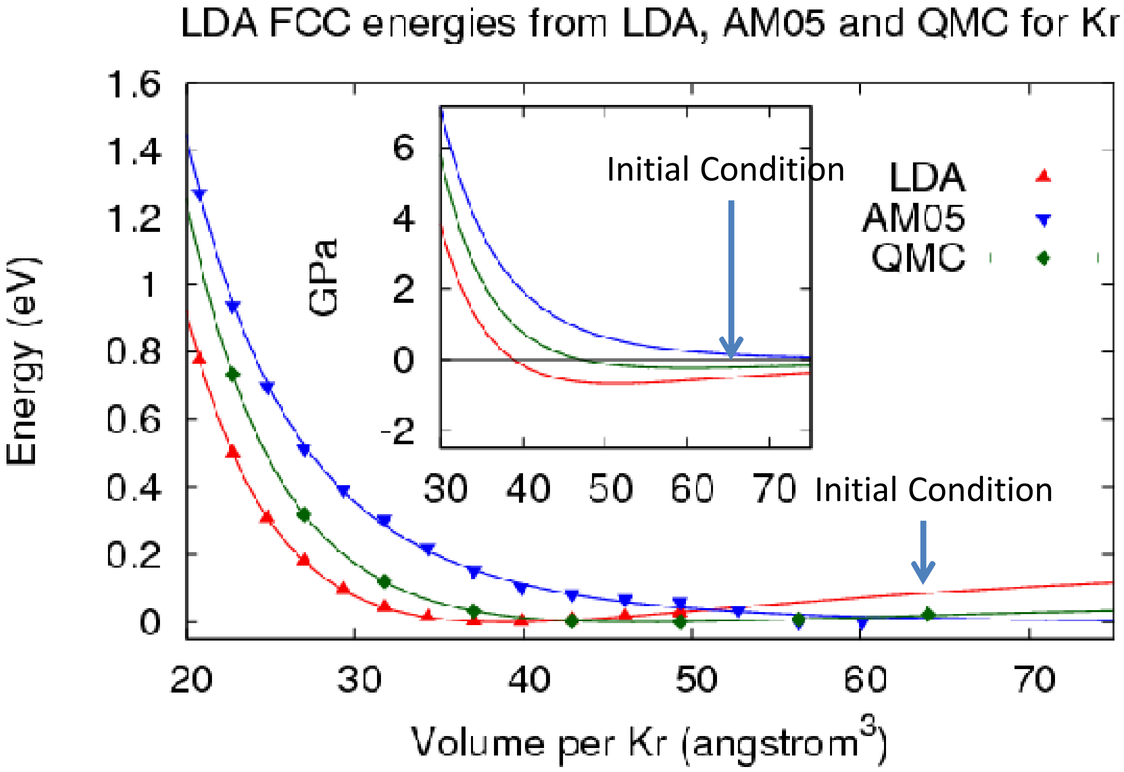
- **Take snapshots from material at initial conditions using QMC with various functionals**
- **Calculate total energies of snapshots with QMC**
- **Compare relative energies**
- **AM05 is better choice**





# Understanding LDA’s failure for low density Kr

- **AM05’s relative success vs LDA can be understood from cold curve**
- **LDA predicts negative pressure at this volume**
- **Negative pressure leads to clumping**
- **AM05 and QMC have positive pressure**



# QMC provides an exciting avenue for understanding materials under extreme conditions

- **Accuracy is consistent across a wide variety of materials and states**
- **Parallel scaling makes QMC appealing for petascale-class supercomputers**
- **Can be used to make an informed choice between DFT functionals**
- **Melting transition can be determined if DFT is "good enough"**
  - **Thermodynamic integration yields higher melt line for Xe**
- **Complex Solid-Solid phase transitions can be examined even where DFT fails**

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