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Diffusion Monte Carlo calculations of xenon and krypton at high pressure

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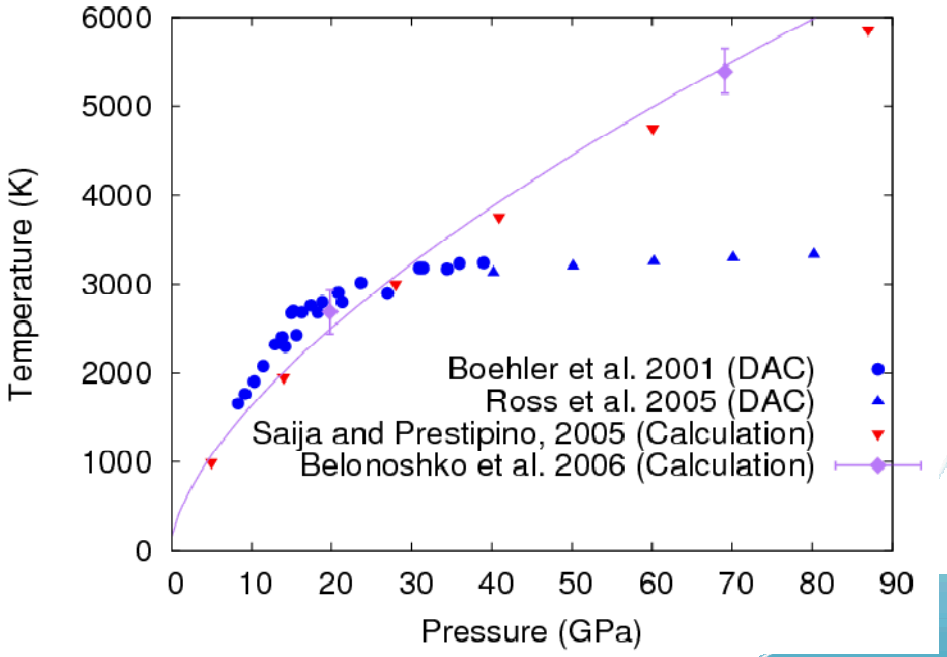
Ab Initio Calculations of Materials under Extreme Conditions (approach from low temperature)

- **Density Functional Theory (DFT)**
  - **Most Common Tool : Generally Successful**
  - **Accuracy Limitations**
    - *Exact functional not known*
    - *New generation functionals have shown large improvements*
  - **Computational Efficiency**
    - *Computationally expensive : 100-1000's of atoms*
    - *Moderate Parallel Scaling*
- **Quantum Monte Carlo**
  - **Potentially higher accuracy than DFT**
  - **Much more computationally expensive**
  - **Nearly perfect parallel efficiency**

Melting of Xe under pressure



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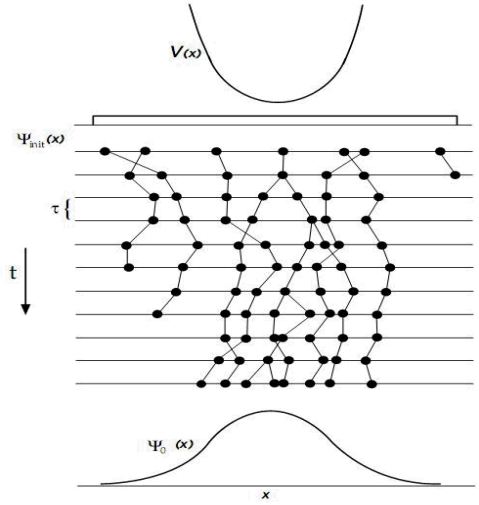
One minute introduction to quantum Monte Carlo

- **Quantum Monte Carlo is an appealing alternative**
  - **Use stochastic projection to solve many body Schrodinger equation exactly**
  - **Only uncontrolled approximation, fixed node approximation, does not involve Hamiltonian (interactions)**
  - **Limitations**
    - *Significantly more expensive than DFT*
    - *Forces not currently available*
    - *Only norm-conserving pseudopotentials*
    - *Only zero temperature electrons*



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

- **Use configurations from quantum MD calculations**
  - **Assess the ability of DFT to determine proper energy landscape**
  - **Use thermodynamic integration approach of Sola et al to estimate change in melting temperature**
    - **Sola and Alfe, PRL. 130, 078501 (2009)**
  - **Assume electronic excitations are treated appropriately within DFT**

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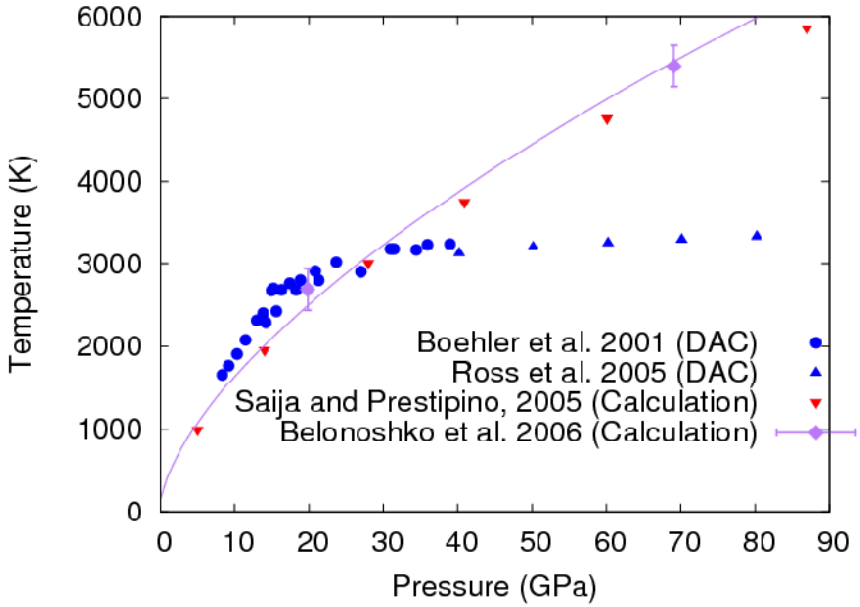
Xe melting: disagreement between DAC and DFT

- **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**
  - **Low number density requires large simulation cells**
  - **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*



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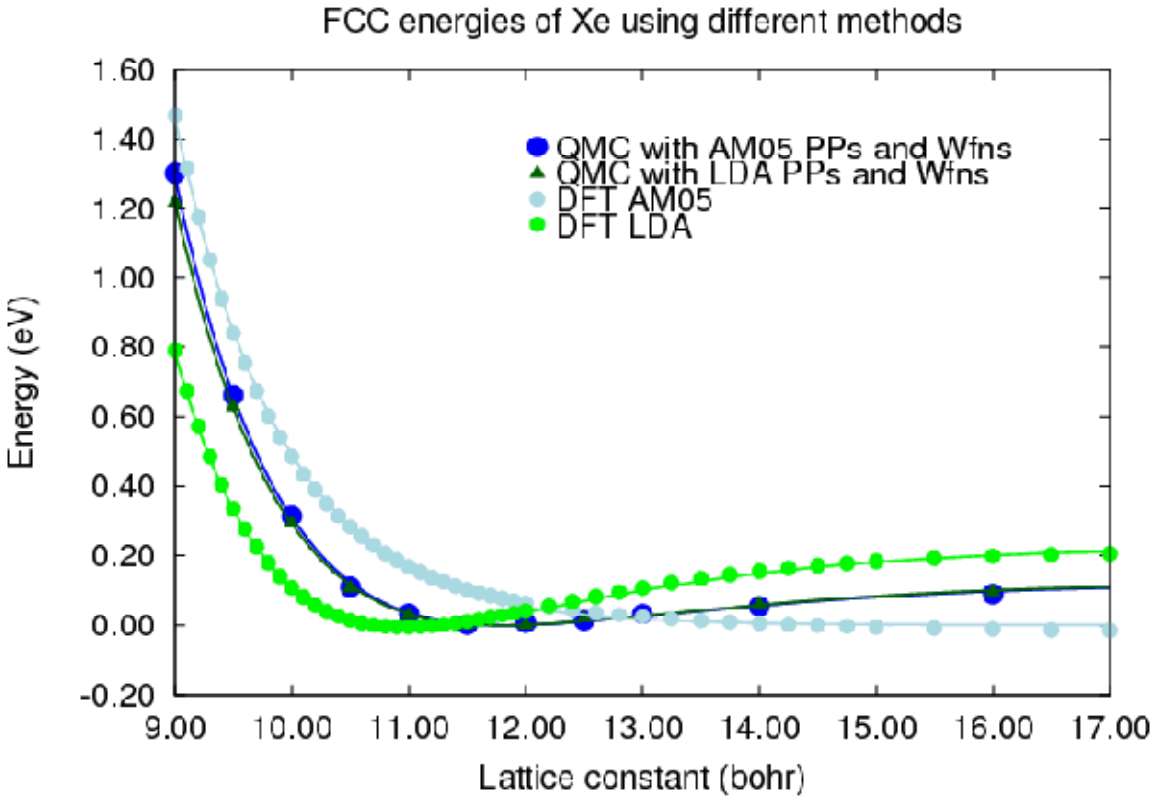
QMC errors are small for solid Xe

- **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*



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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**

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

- **The change in melting temperature between DFT and DMC is**

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

- **Assume that difference in dynamics between DFT and DMC is small (fluctuation terms above are small)**
- **Extract snapshots from liquid and solid phase and calculate change in melting temperature**

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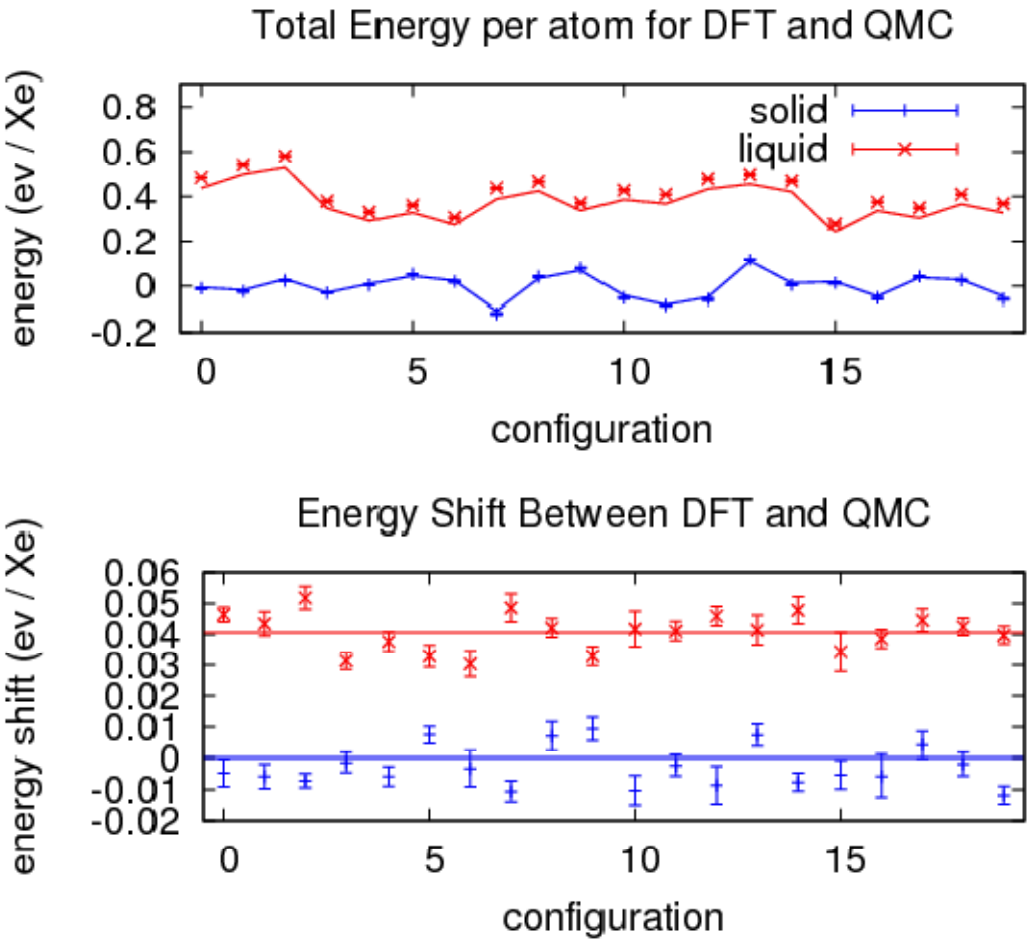
DMC calculations of solid and liquid snapshots

- **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**
- **Assuming a rigid shift of the enthalpy curves → Increase in melting temperature by 470 +/- 30 K at 73 Gpa**
- **Magnitude of correction similar to Sola and Alfe. PRL 130, 078501 (2009)**



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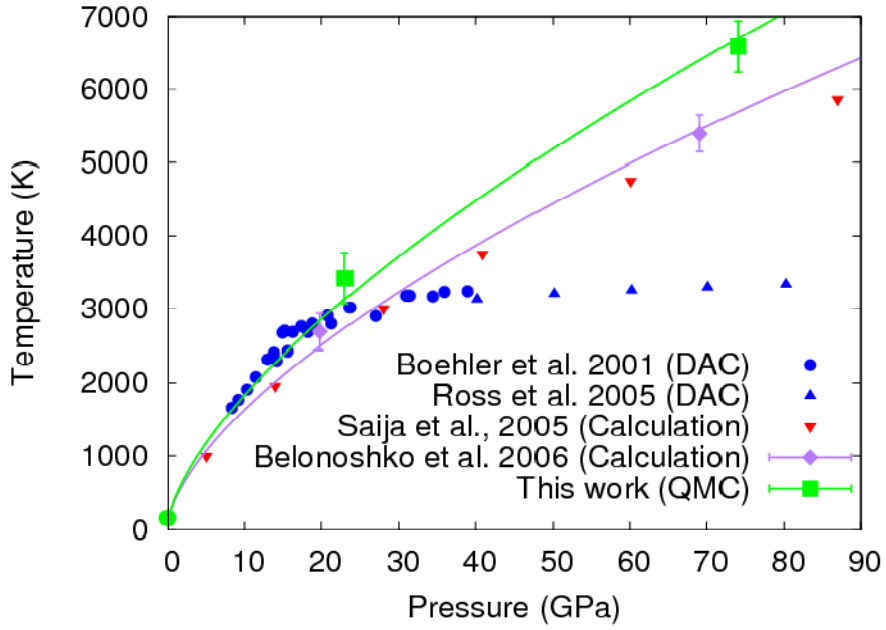
QMC revised melt curve for Xe:

- **We found that diffusion Monte Carlo can accurately treat Xe under pressure**
  - **Pseudopotential Approximation is small**
  - **Fixed node approximation is likely a small error**
- **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**



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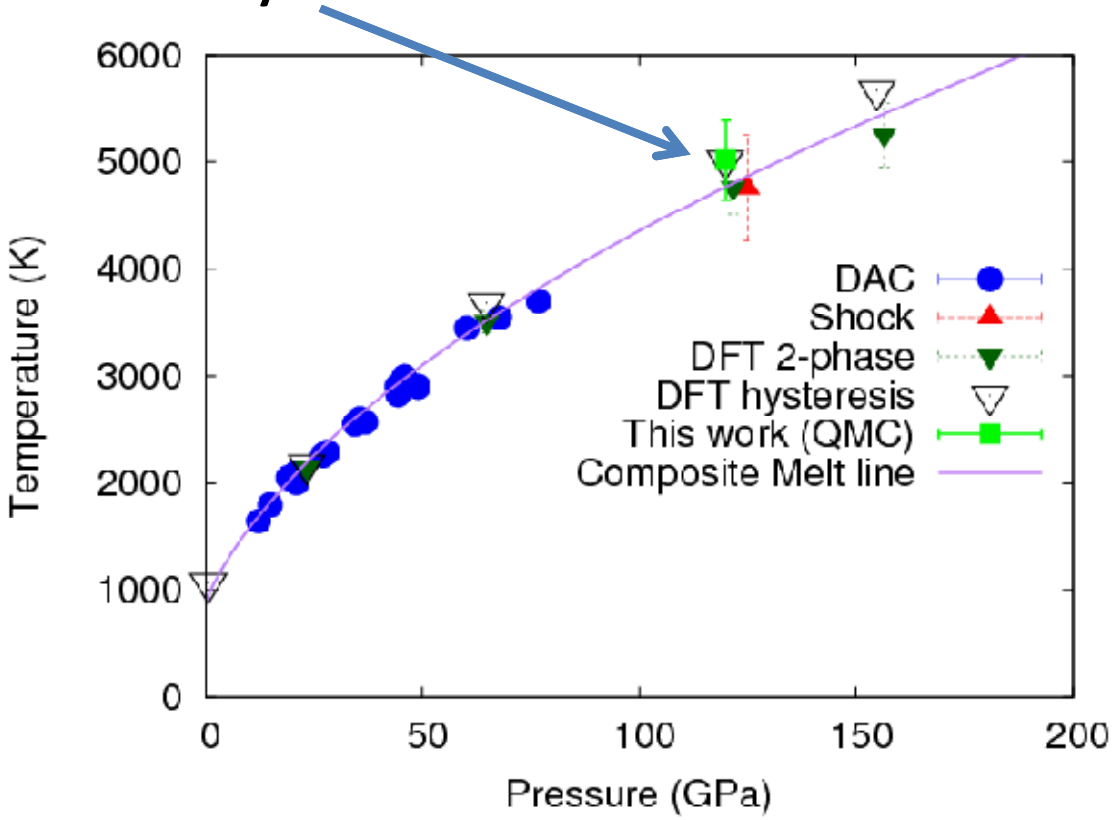
Validation of Method: Melting of Aluminum

- **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 !**



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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**

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.

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

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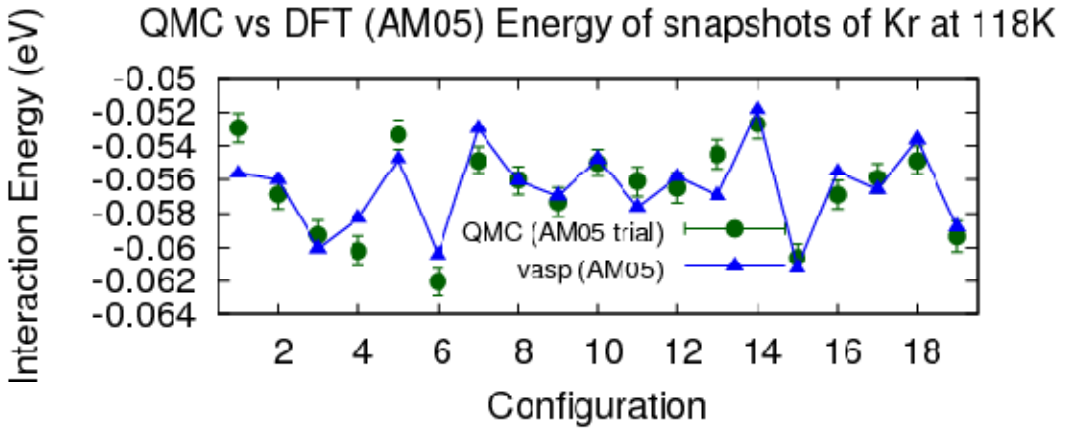
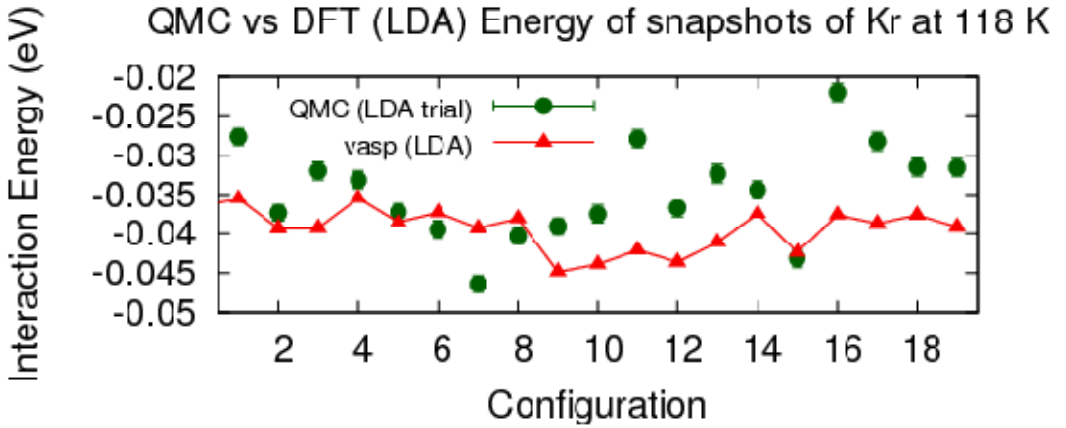
LDA a poor choice for initial condition of Kr Hugoniot

- **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**





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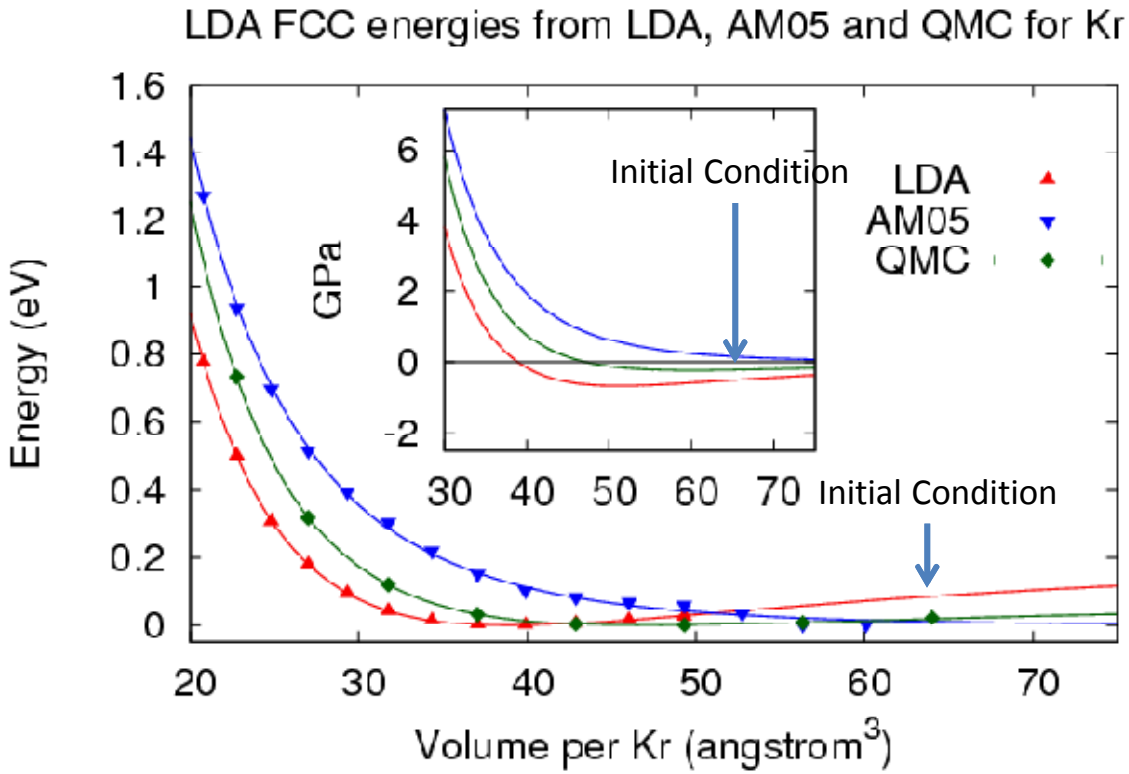
Understanding LDA's failure for low density Kr

- **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**



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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

Acknowledgements

- John Carpenter
- Kyle Cochrane
- Jeongnim Kim
- Sandia High Performance Computing
- ACES

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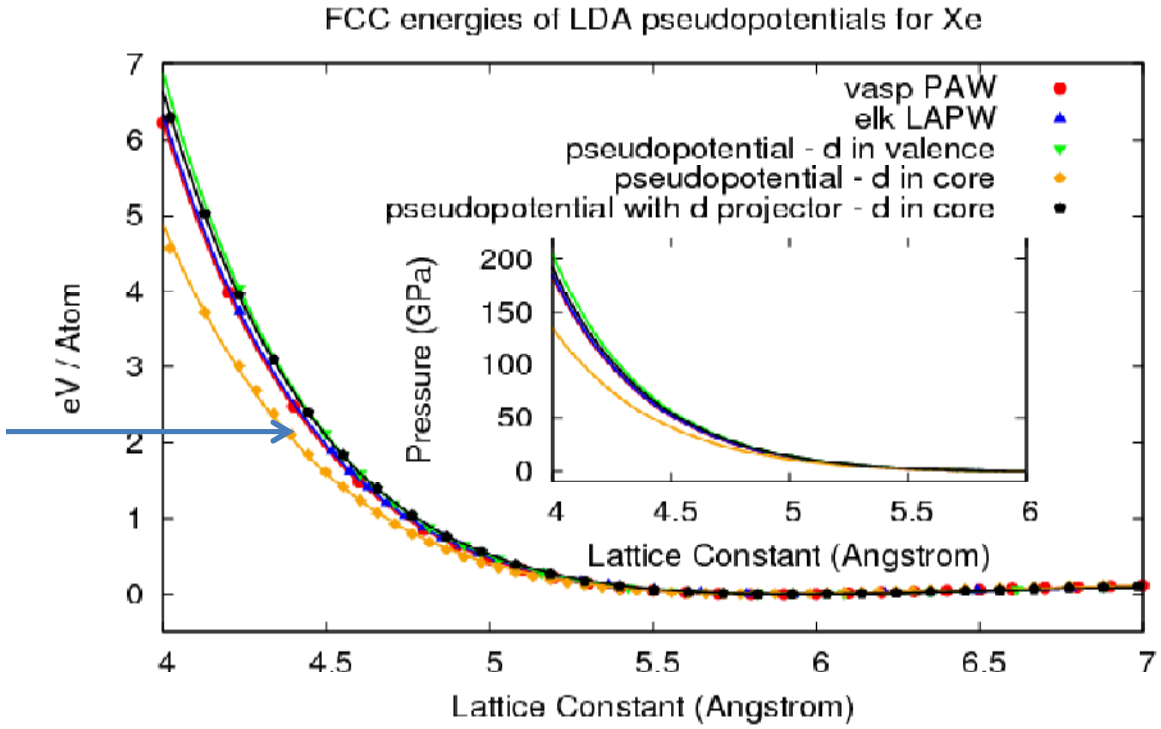
Importance of pseudopotential in QMC

- **Must strip out core electrons to make problem computationally tractable**
  - **Core does not contribute to chemistry at these pressures**
- **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



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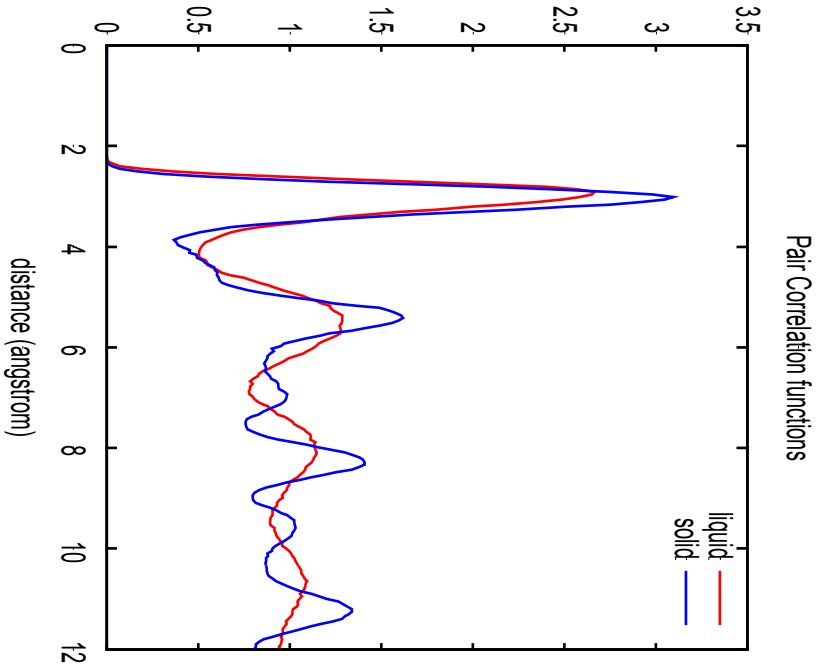
Generating Snapshots with DFT

- **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**



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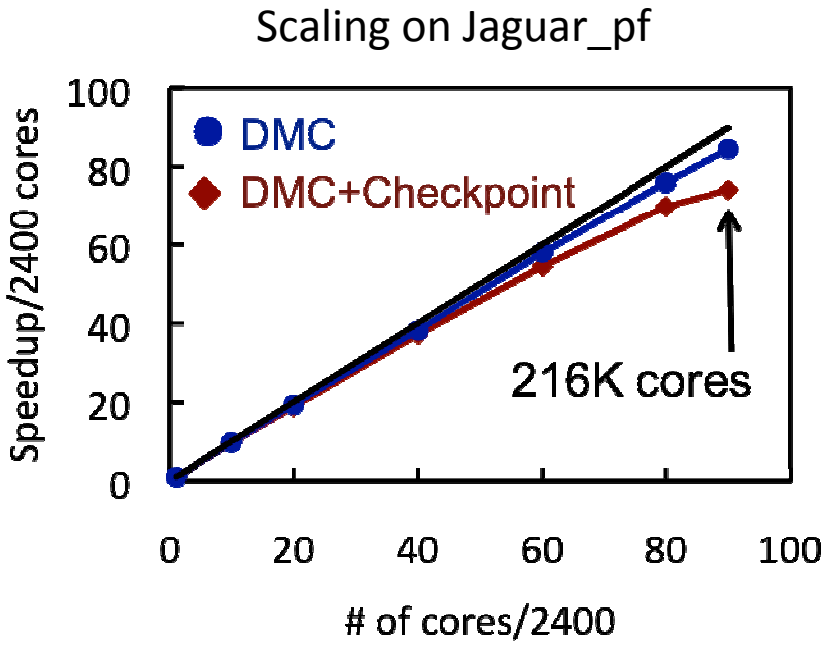
QMCPACK – Massively Parallel QMC

- 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
- GPU port to CUDA with 15X speedup



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