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Diffusion Monte Carlo calculations of xenon melting under pressure

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Xenon: Rare gas with rare behavior under pressure

- **Closed shell insulator at ambient conditions**
- **Under static compression**
  - **FCC -> HCP Phase transition**
  - **Isostructural insulator to metal transition**
- **Can form compounds with H_2 under pressure**
  - **Somayazulu et al. Nature Chemistry 2, 50 (2010)**
- **Liquid phase may exhibit anomalous behavior**
  - **Very narrow temperature range at ambient pressure**
  - **Potentially flat melt curve at moderate pressures**

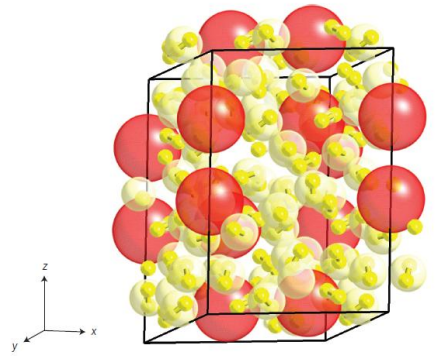
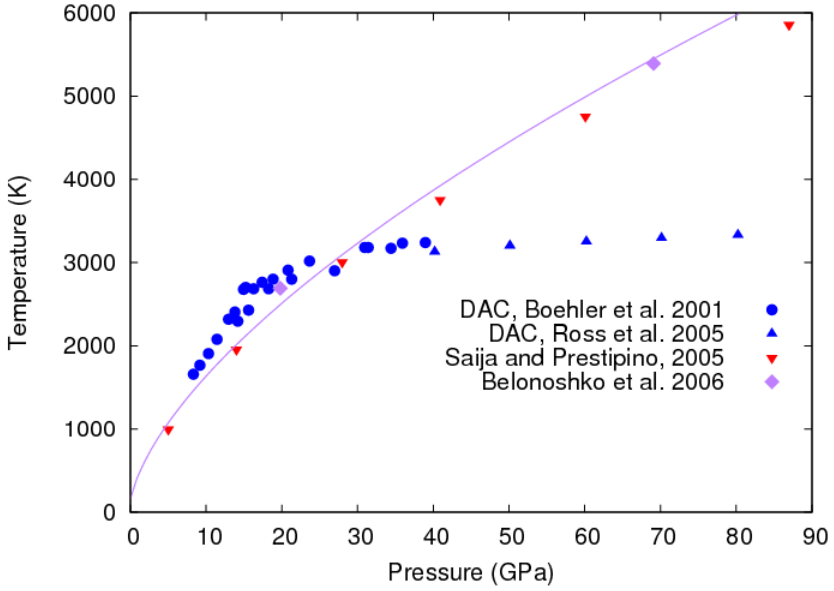


Figure 3 | Model structure of $Xe(H_2)_7$. The xenon atoms are surrounded by dumbbell-shaped, freely rotating hydrogen molecules represented by the spherical shells.



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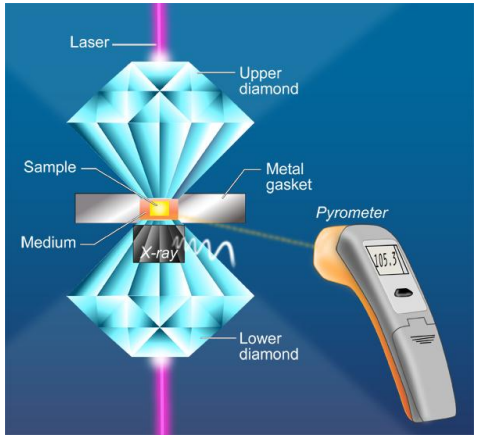
Xe melting: disagreement between DAC and DFT

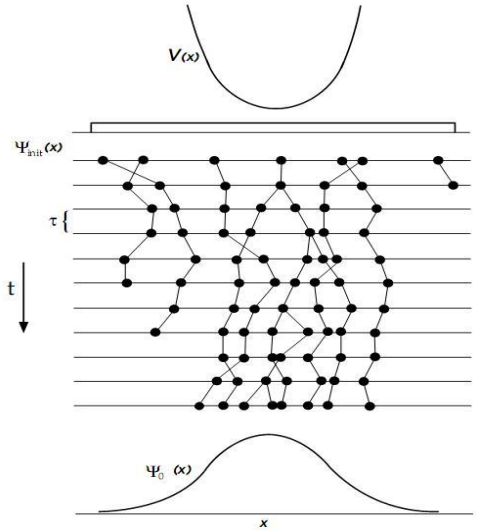
- **Disagreement between melting under pressure between DAC, ab initio calculations and shock measurements is common**
  - **See for example Ta, Fe, MgO and Xe**
- **Many sources of uncertainty**
  - **DAC**
    - *Anisotropic Stress, Reactivity, Ambiguous Phase Assignment*
  - **Shock**
    - *Temperature 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*



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

Assessing Quantum MD melting with 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*



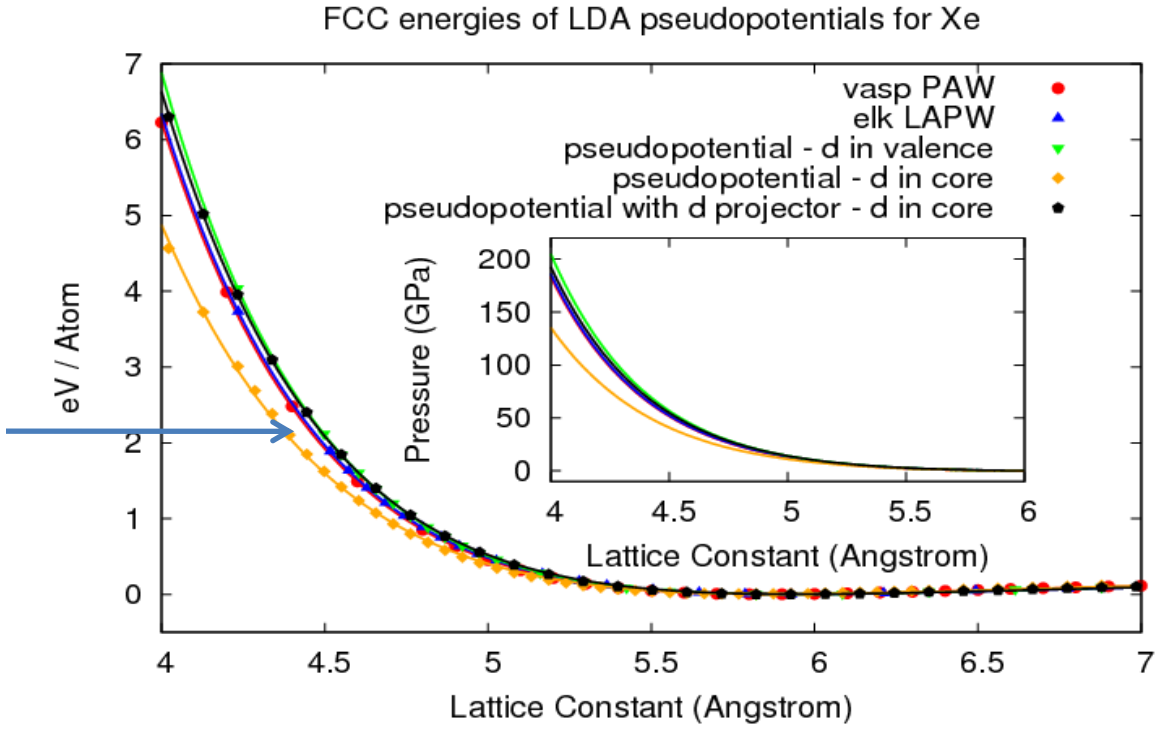
J. Needs, M. D. Towler, N. D. Drummond, and P. Lopez-Rios, Casino Version 2.2 User Manual, University of Cambridge , Cambridge (2008)

- **Use snapshots 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**

Importance of pseudopotential in QMC

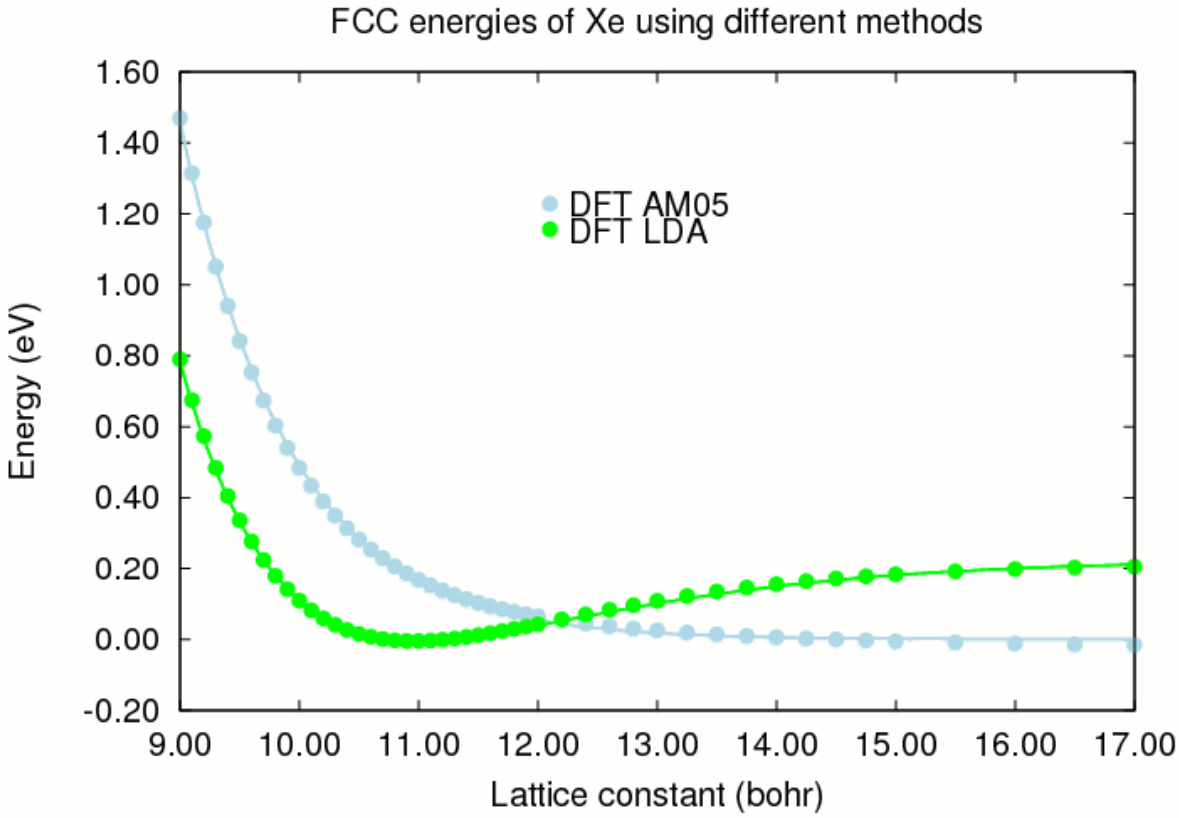
- **Must strip out core electrons to make problem computationally tractable**
  - **Core does not contribute to chemistry at these pressures**
- **Validated norm conserving Xe pseudopotentials not widely available**
- **D-states well removed from valence, but d-projector is crucial**
  - **Increasing d-hybridization suggested as cause of flat melt line**
    - *Ross et al. PRL 95. 257801 (2005)*

~0.5 eV / Xe difference at 70GPa



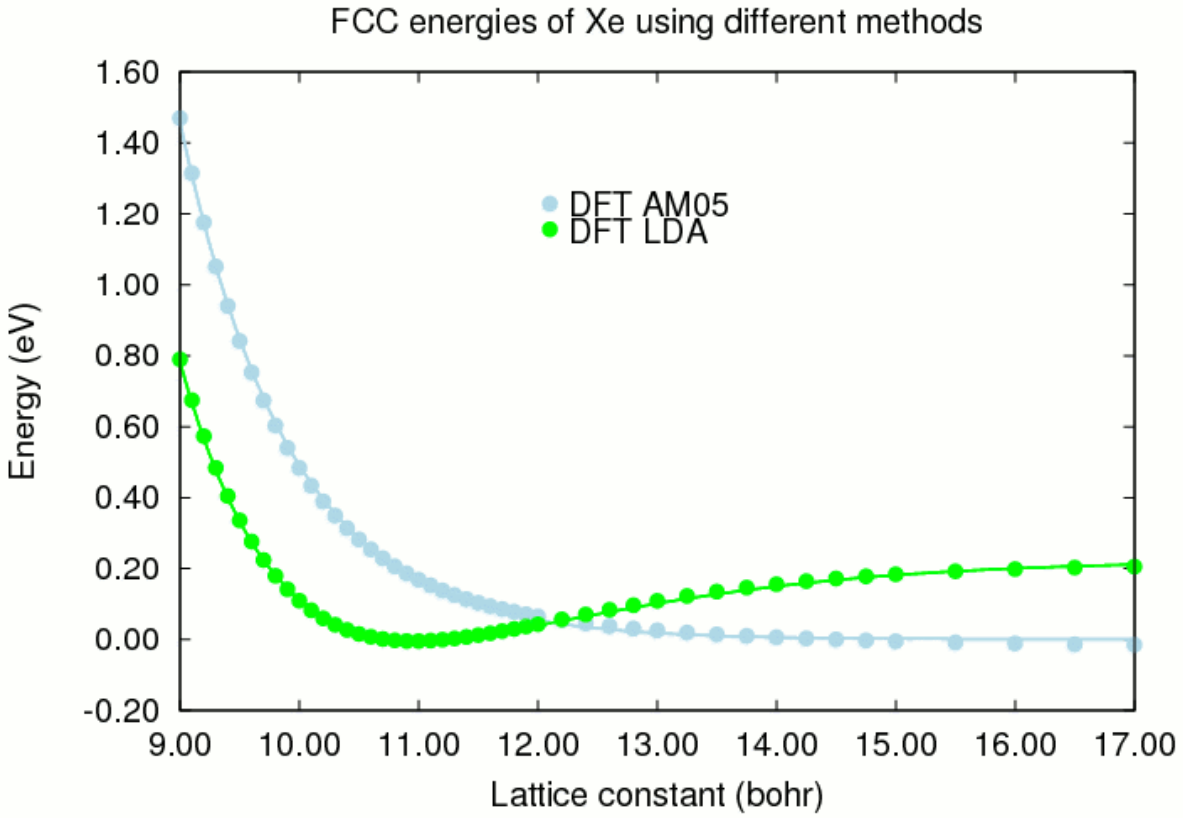
Fixed node approximation and DFT Functional

- **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*



Thermodynamic Integration approach to melting

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

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

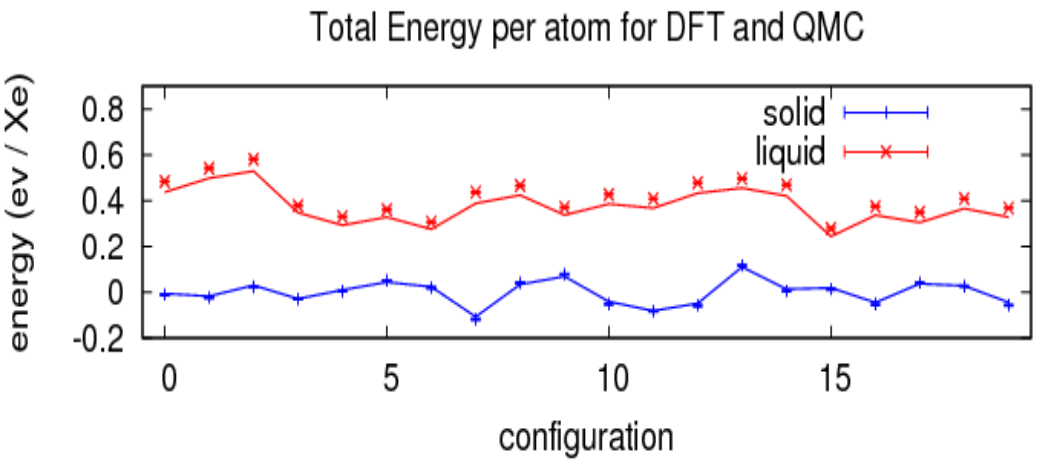
- **The change in melting temperature between DFT and DMC is**

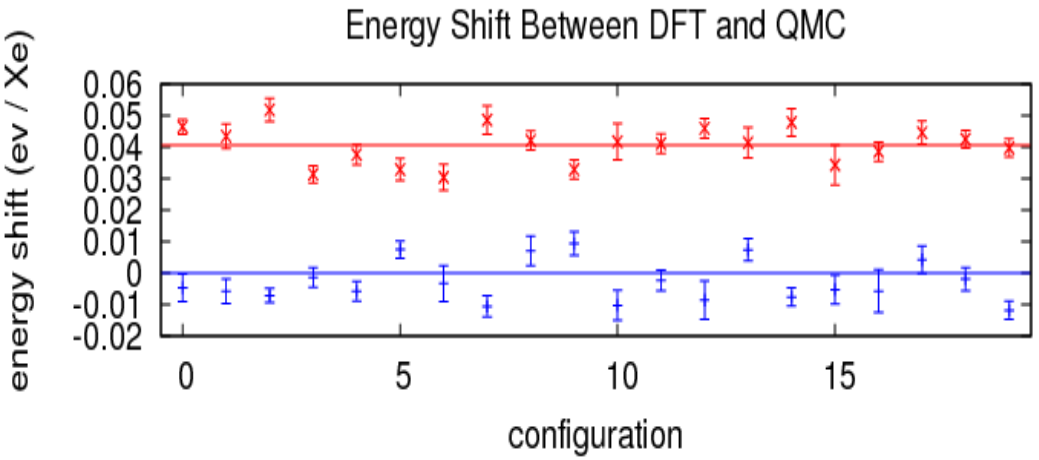
$$\Delta T_m \approx \frac{\Delta G^{ls}}{S^{ls}_{DFT}} \qquad \Delta G \approx \Delta F - V\Delta p^2 / 2K_T$$

- **Assume that difference in dynamics between DFT and DMC is small (fluctuation terms above are small)**
- **Take two long molecular dynamics calculations at coexistance with electronic temperature equal to ionic temperature**
- **Extract snapshots from liquid and solid phase and calculate change in melting temperature**

DMC calculations of sold and liquid snapshots

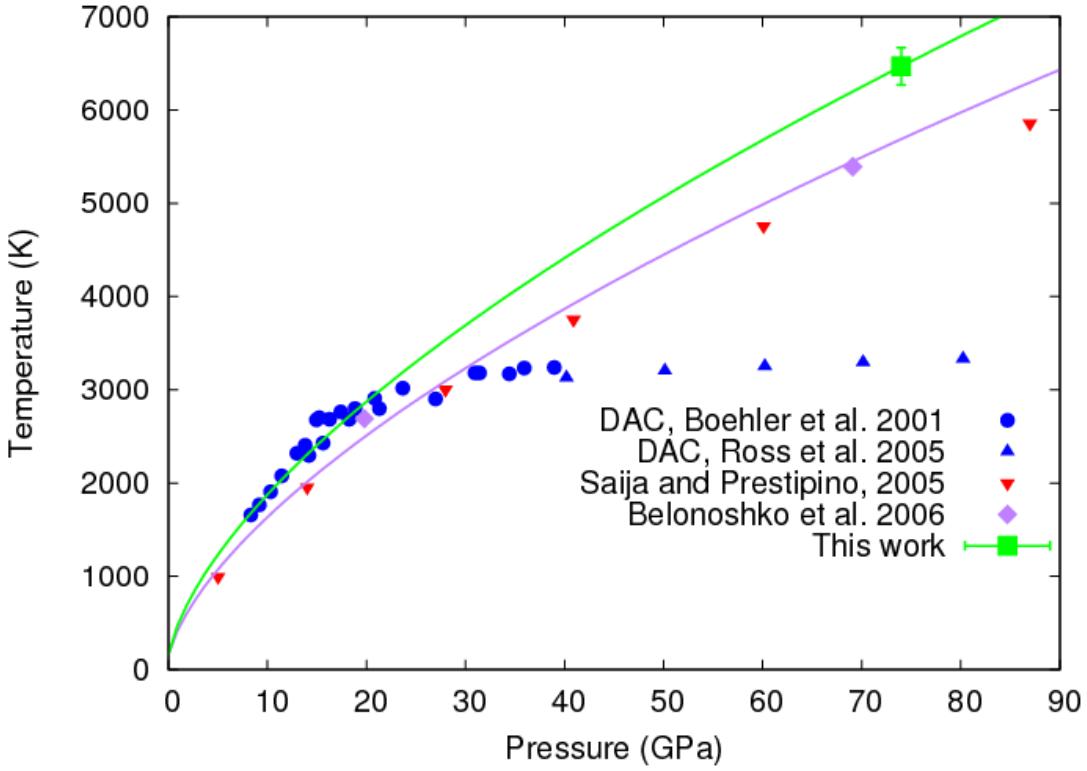
- 20 snapshots from 108 atom solid and liquid LDA runs at 6000 K
- Fluctuations of QMC energy about LDA energies are small
- Energy difference between liquid and solid 0.0406 +/- 0.0027 eV / Xe greater in DMC
- Assuming a rigid shift of the enthalpy curves → Increase in melting temperature by 470 +/- 30 K at 73 Gpa
- Magnitude of correction similar to Sola and Alfe. PRL **130,** 078501 (2009)





Conclusions

- **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 near 1 Mbar**
- **Errors in total energies from DFT/LDA will increase melting temperature**



QMC Calculation Details

- Trial wavefunctions for qmcpack using hybrid LMTO like and b-spline representation - 22 GB of memory per node for the wavefunction
- Slater-Jastrow form used with independent one body jastrow factors for each Xe and an overall two body jastrow
- Each DMC calculation required 15,000 CPU hours
- Timestep (0.01 Ha) converged to within 0.0001 Ha / Xe
- Finite size correction using MPC and Chiesa corrections