Quantum Monte Carlo Study of the Elastic Instability of Stishovite Under Pressure

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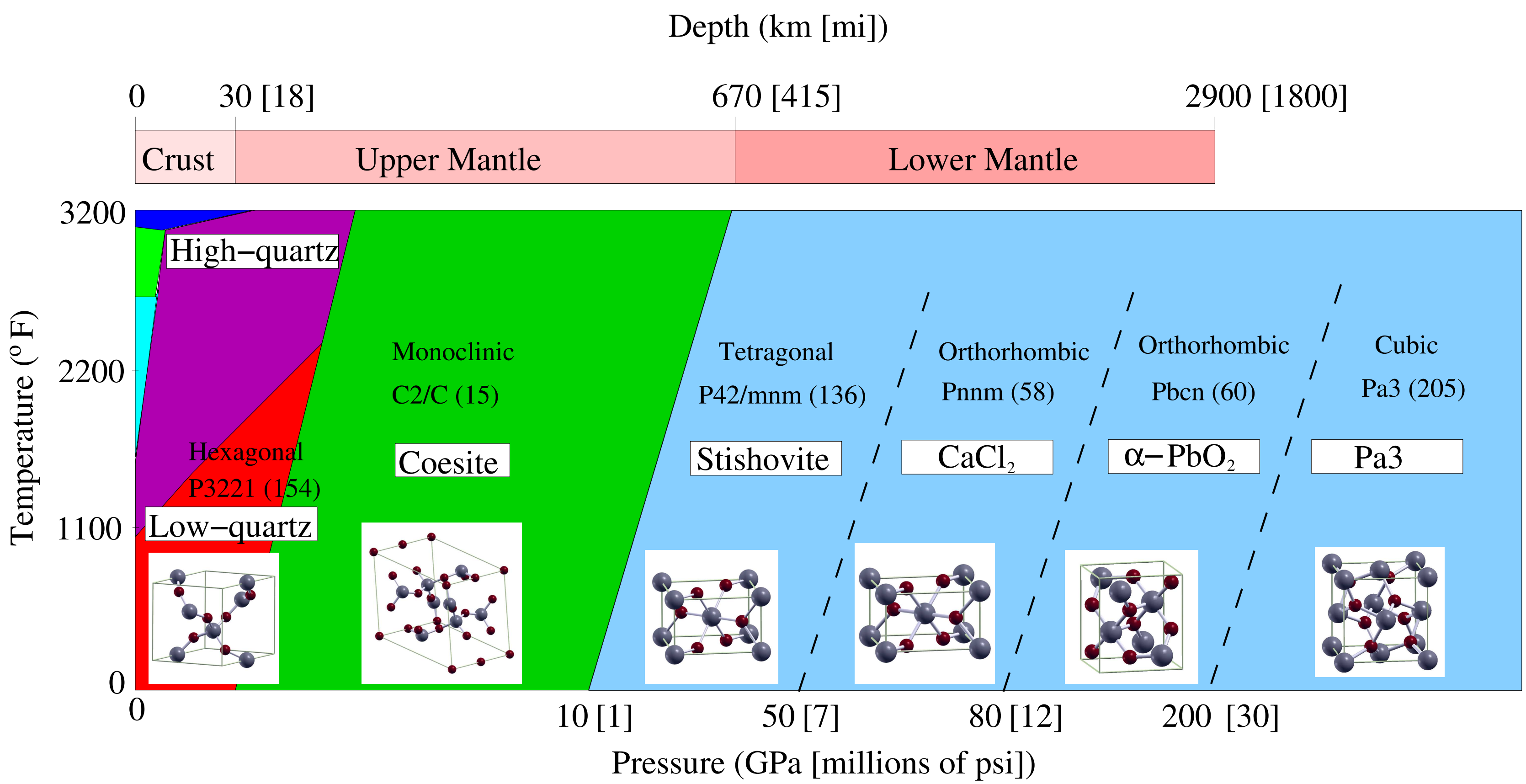
Outline

1. Stishovite is a high pressure crystal phase of silica (SiO_2), forming near 10 GPa.
   - It is a common, rutile-structured silicate, representative of many Earth minerals.

2. Direct observation of deep Earth minerals is currently impossible.
   - Computational modeling complements seismic and high pressure experiments.
   - DFT, while powerful in many cases, can unexpectedly make false predictions.
   - QMC, while more accurate and reliable than DFT, is often 100-1000 times more costly.

3. The first QMC computations of elastic constants demonstrate its feasibility for geophysics applications.
   - QMC correctly predicts the softening of stishovite's elastic shear modulus under pressure.
   - Over a pressure range of 0 to 50 GPa, the elastic modulus softens from 270 to 0 GPa.
   - The elastic instability drives a transition to a $CaCl_2$-type phase.

The silica phase diagram is rich in physics



- Near 10 GPa silica becomes very dense as the coordination changes from four to six-fold.
- Natural stishovite has been found on Earth's surface near meteor craters.
- Synthetic stishovite was first made in a diamond anvil cell from quartz in 1960 (Stishov).
- Stishovite in deep Earth has been inferred from seismology and diamond inclusions.
- Stishovite's elastic shear modulus becomes unstable at 50 GPa, transitioning to $CaCl_2$.

$CaCl_2$ - Tsuchida 1989; α-PbO_2 - Dubrovinsky 1997; Pa3 - Kuwayama 2005

Comparison of DFT and QMC methodology

Density Functional Theory (DFT)

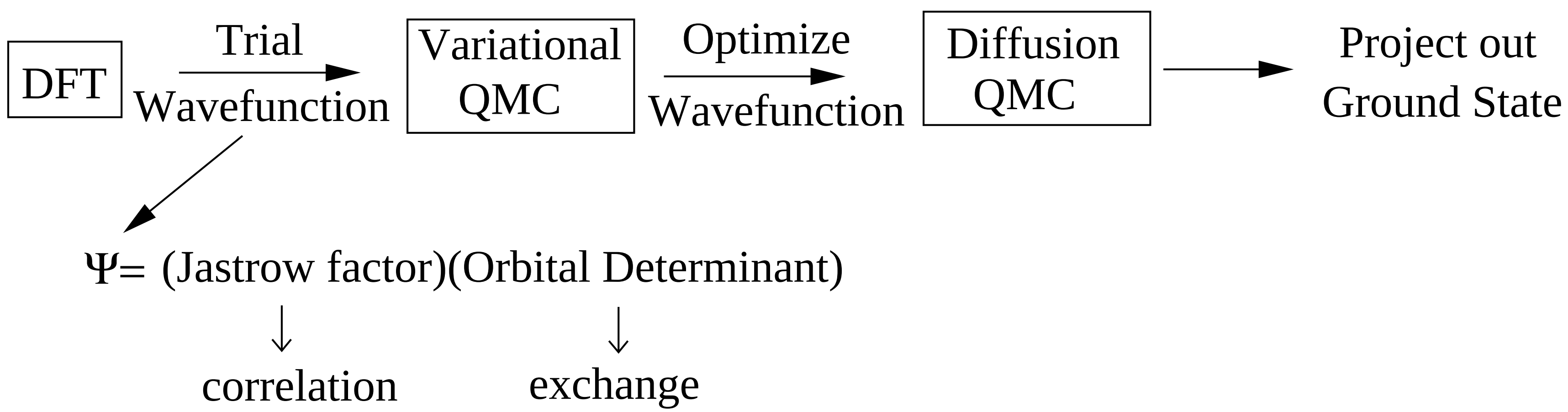
- Many-body wave equation is mapped onto a single-electron problem.
- Effective one-electron potential is a function of ground state electron density.
- Ground state properties are obtained by minimizing E[n(r)]:

$$E[n(r)] = T[n(r)] + E_{ee}[n(r)] + E_{xc}[n(r)]$$

- Exchange-correlation functional is unknown - approximate as LDA, GGA, ect.

Quantum Monte Carlo (QMC) (see Foulkes, Rev. Mod. Phys. 73, 33 (2001))

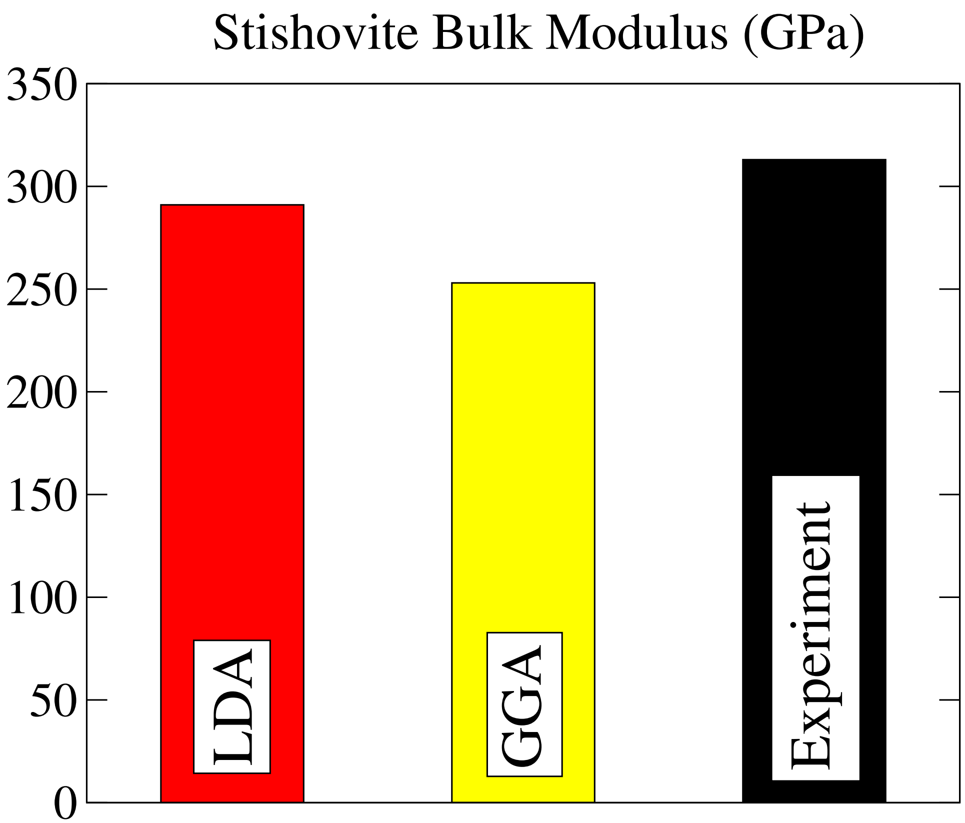
- Uses Monte Carlo techniques to solve the full many-body wave equation.
- Explicitly computes exchange and correlation of electrons.

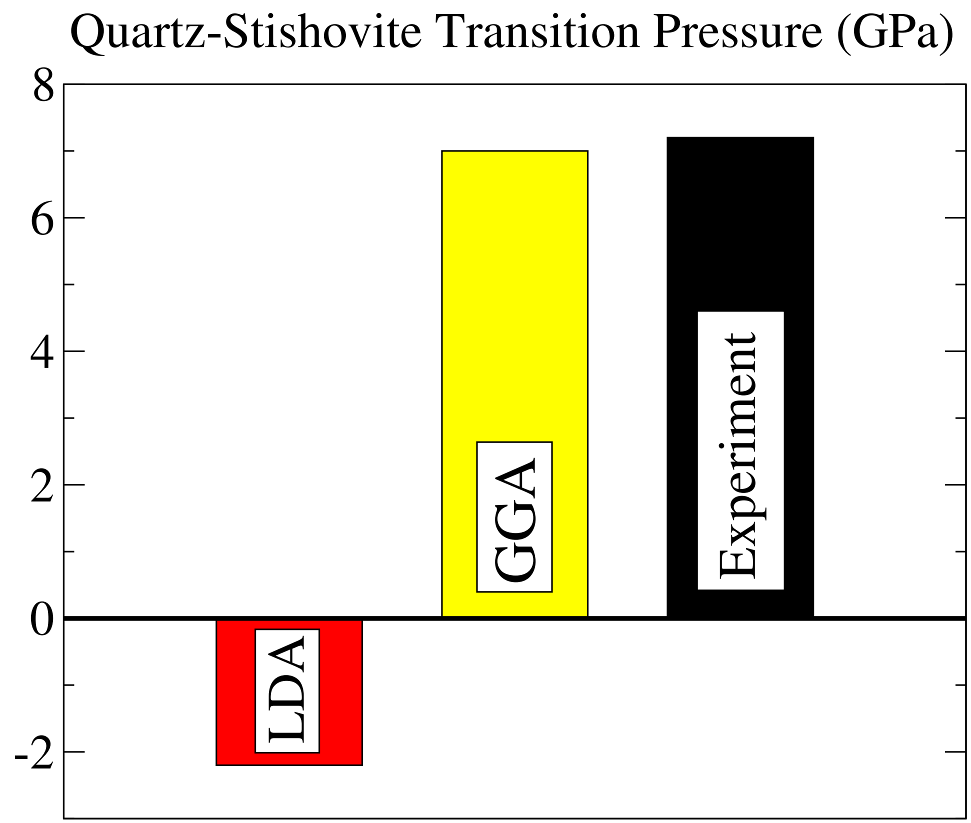


For the experts:

- CASINO code: pseudopotentials, b-spline basis, mpc finite size correction, 2x2x3 supercells.

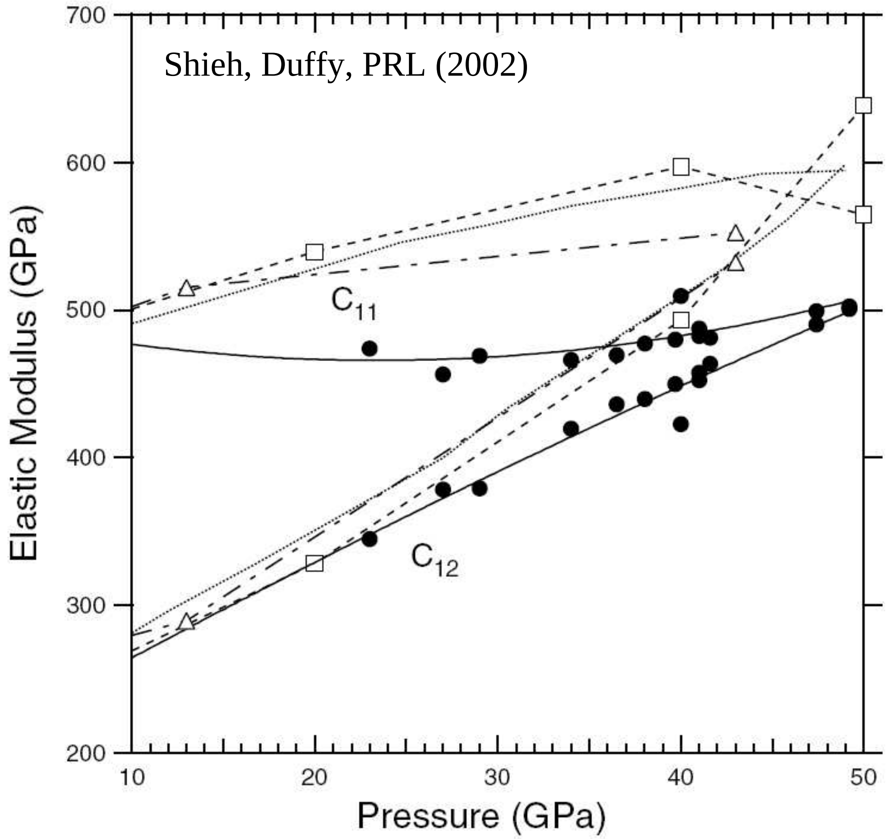
DFT can unexpectedly fail due to choice of XC-functional

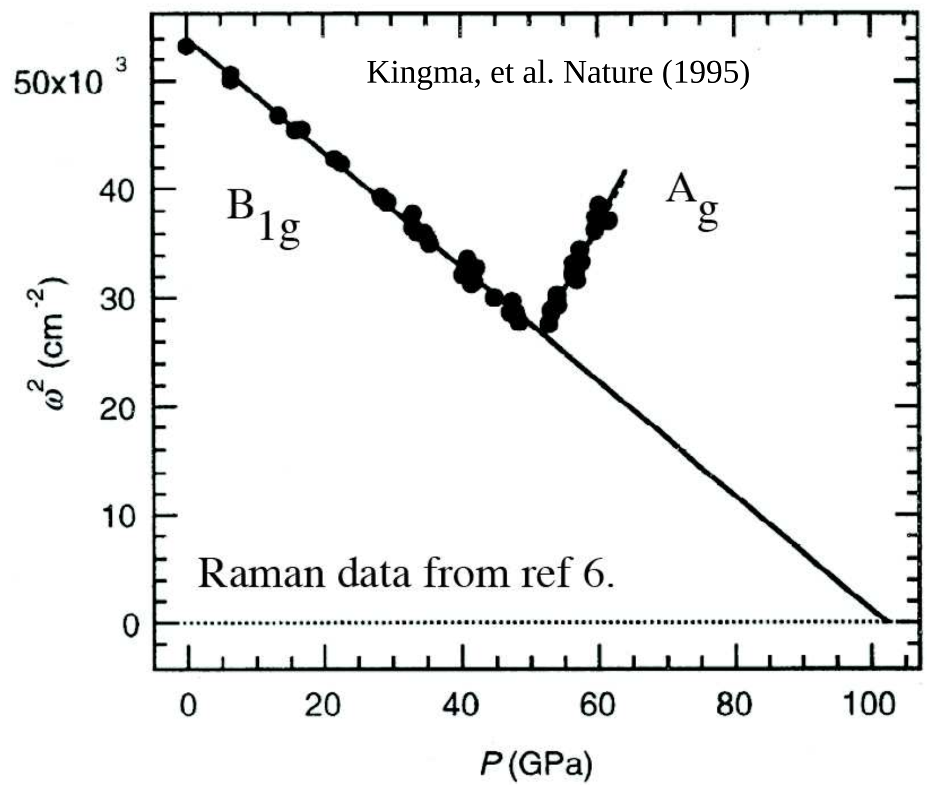




- LDA typically predicts silica structural properties (bulk modulus, lattice constant, and elastic constants) well.
- However, LDA fails to correctly predict the quartz-stishovite phase transition.
- GGA functionals tend to do a better job predicting energies, and worse on structural properties than LDA.
- QMC affords more reliability since it formally computes exchange and correlation.

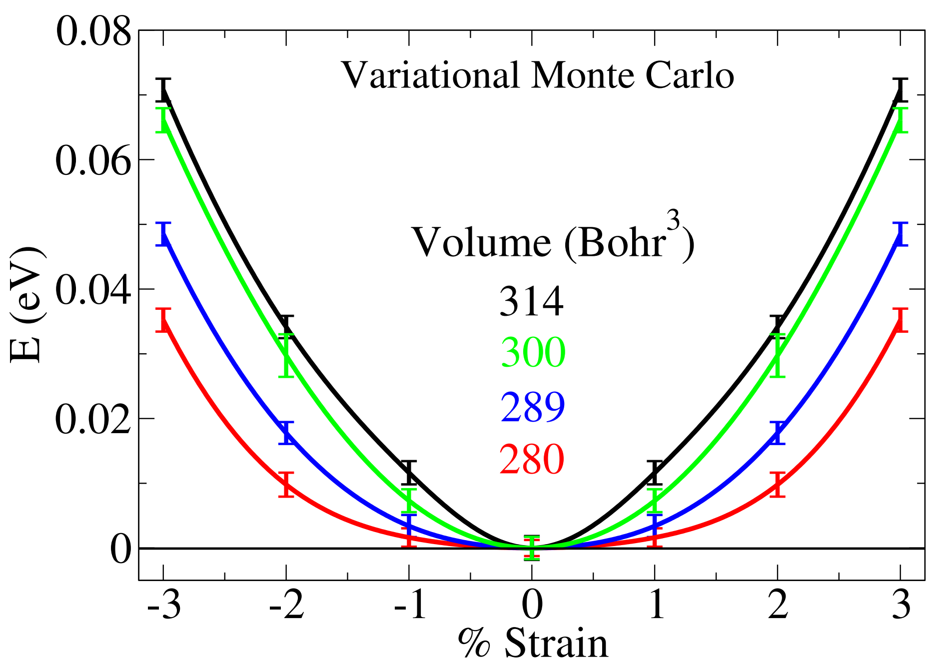
Elastic softening drives the stishovite to $CaCl_2$ phase transition





- Softening of the elastic shear modulus c_{11}-c_{12} and B_{1g} Raman mode predicted by LDA (Cohen 1991, 1992).
- Tetragonal stishovite transforms to orthorhombic $CaCl_2$ near 50 GPa, where c_{11}-c_{12} and B_{1g} vanish.
- The softening has geophysical relevance in its effect on seismic wave velocities.
- The softening is a simple, well documented example to test the feasibility of QMC to predict elastic constants.

Elastic constants are computed by straining the crystal lattice



Strain-Energy Density relation

Strain the lattice:

$$R' = [I + \epsilon]R$$

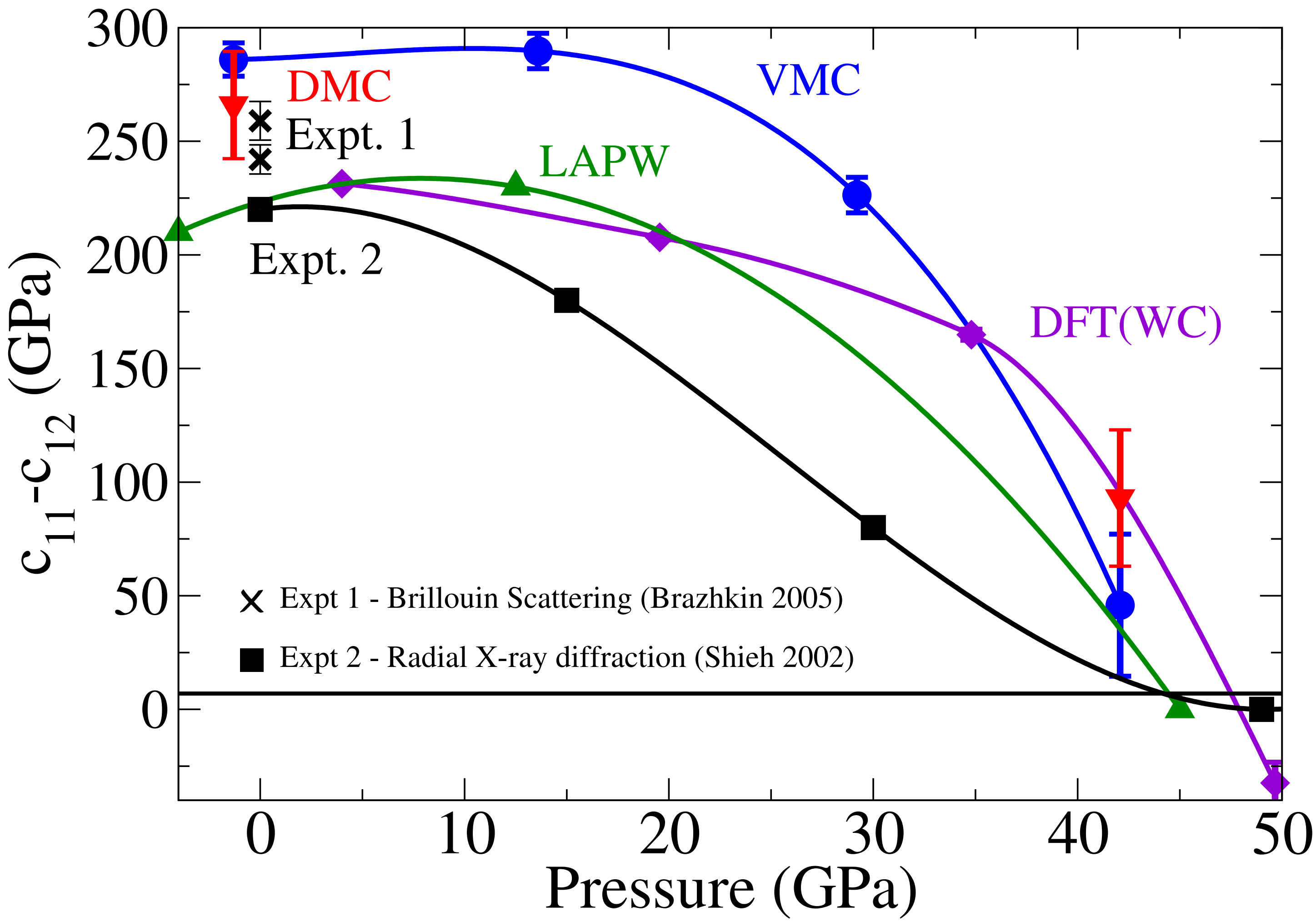
For a volume conserving strain:

$$\frac{\Delta E}{V} = \frac{1}{2} c_{ijkl} \epsilon_{ij} \epsilon_{kl}$$

$$c_{ijkl} = \frac{1}{V} \frac{\partial^2 E}{\partial \epsilon^2}$$

- Curvature of energy varied with strain is proportional to the elastic constants.
- Energies computed at several volumes determine variation of elastic constants with pressure.
- Good estimates of the curvature in QMC require small statistical error bars on energies.
- QMC computation at 4 volumes in VMC and 2 volumes in DMC used 3 million cpu hours.

QMC elastic constants compared with DFT and experiment



- Both DFT and QMC predict the shear modulus vanishes near 50 GPa.
- Radial X-ray values tend to lie below theoretical values.
- DMC agrees best with Brillouin scattering at zero pressure.
- Intermediate DMC pressures were avoided only to save cpu time.

Conclusions

• Stishovite is a six-fold coordinated phase of silica expected to exist in the lower mantle.

• Elastic softening, first predicted by DFT, has indicated sound velocities in stishovite are possibly in agreement with measured seismic velocities.

• DFT, while often accurate, can unexpectedly fail due dependence on choice of exchange-correlation approximation.

• QMC is a accurate and reliable alternative to DFT when CPU time is not prohibitive.

• This talk presents the first QMC computation of elastic constants.

• QMC successfully predicts the shear elastic constant softening in stishovite and the transition to $CaCl_2$ at 50 GPa, which confirms previous DFT and experimental results.