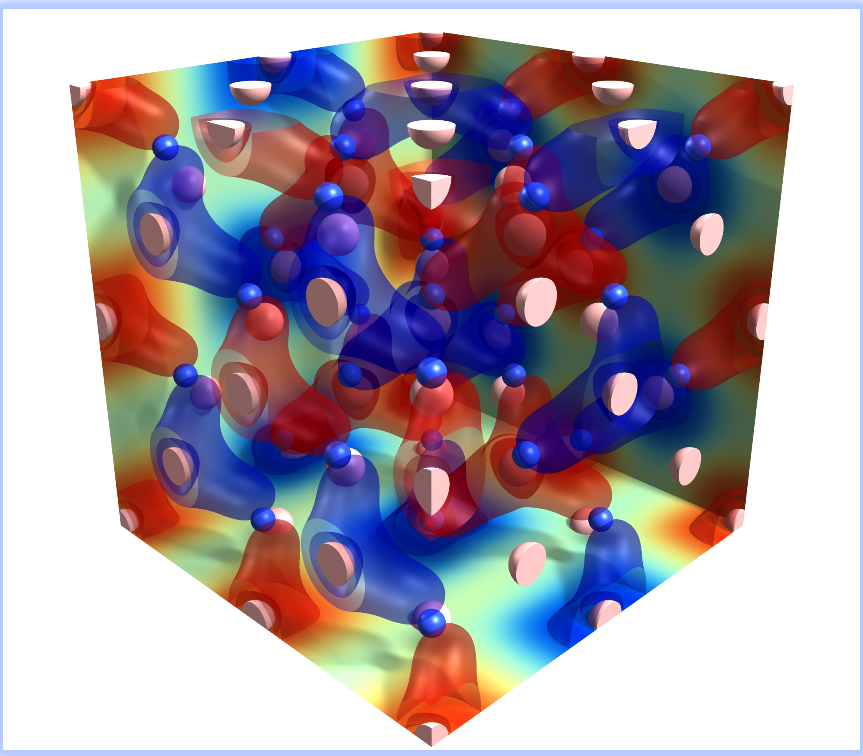
Quantum Monte Carlo Calculations of Solids



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The is a team effort. We acknowledged invaluable contributes from:

- Ken Esler, Jeongnim Kim, David Ceperley (UIUC)
- R. E. Cohen (Carnegie Institution of Washington)
- K. P. Driver, J. W. Wilkins (Ohio SU)
- P. López Ríos, M. D. Towler, R. J. Needs (Casino team, Cambridge)
- Steven Stackhouse and Hugh Wilson (UC Berkeley)
- Richard Hennig, Cyrus Umrigar (Cornell)

How does Quantum Monte Carlo Work?

$$\hat{H}\Psi(\mathbf{R}) = [\hat{T} + \hat{V}]\Psi(\mathbf{R}) = \left[-\sum_{i=1}^{N} \frac{\hbar^2}{2m_i}\nabla^2_{\mathbf{r}_i} + \sum_{i>j}^{N} \frac{Z_i Z_j}{|\mathbf{r}_i - \mathbf{r}_j|} \right] \Psi(\mathbf{R}) = E\Psi(\mathbf{R}),$$

Project out the many-body ground-state wave function:

$$e^{-\tau\hat{H}}\psi_T(R) = e^{-\tau\hat{H}}\left[a_0\psi_0 + a_1\psi_1 + a_2\psi_2 + \ldots\right]$$

$$= \underbrace{a_0 e^{-\tau E_0}\psi_0}_{\text{Increased weight}} + \underbrace{a_1 e^{-\tau E_1}\psi_1}_{\text{Reduced weight}} + \underbrace{a_2 e^{-\tau E_2}\psi_2}_{\text{Reduced weight}} + \ldots$$

Approach the ground state iteratively:

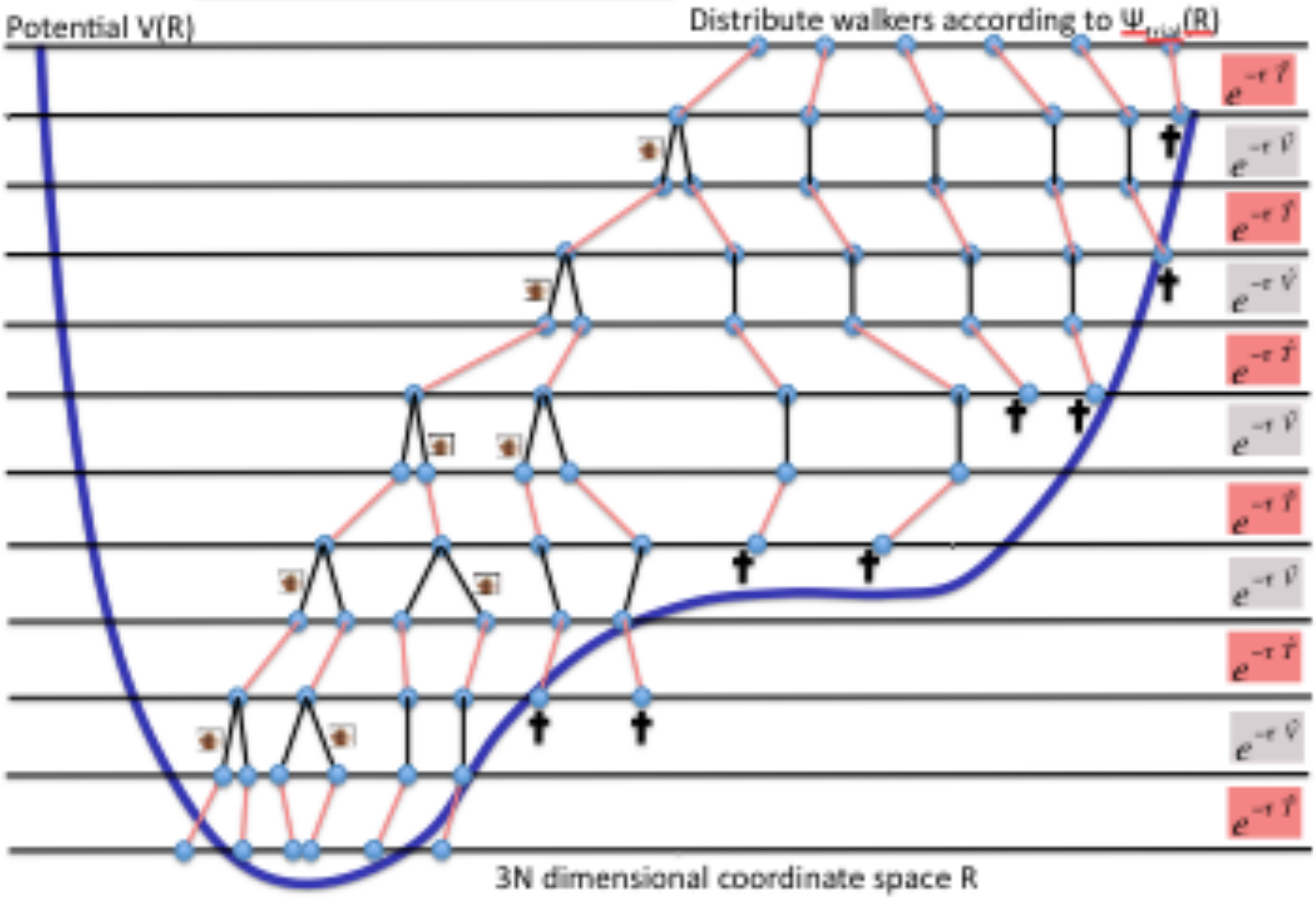
$$\psi_{i+1}(R) = e^{-\tau\hat{H}}\psi_i(R)$$

$$\lim_{i\to\infty} \psi_i(R) = \psi_0(R)$$

For small time steps, τ, split the kinetic and potential operators:

$$e^{-\tau\hat{H}} \equiv e^{-\tau(\hat{T}+\hat{V})} \approx e^{-\tau\hat{T}} e^{-\tau\hat{V}} e^{-O(\tau^2)}$$

Illustration of QMC



Trial Wave Function for High Efficiency and Fermion nodes

$$\Psi(\mathbf{R}) = e^{J(\mathbf{R})} D^{\uparrow}(\mathbf{r}_1, \ldots, \mathbf{r}_{N_\uparrow}) D^{\downarrow}(\mathbf{r}_{N_\uparrow+1}, \ldots, \mathbf{r}_N)$$

Approximations in current QMC calculations:

- Slater determinant is constructed from DFT orbitals
- Geometries may be taken from DFT
- Pseudopotentials are used in most cases

Three recent QMC Applications

1) Addressing the DFT band gap problem illustrated for solid helium

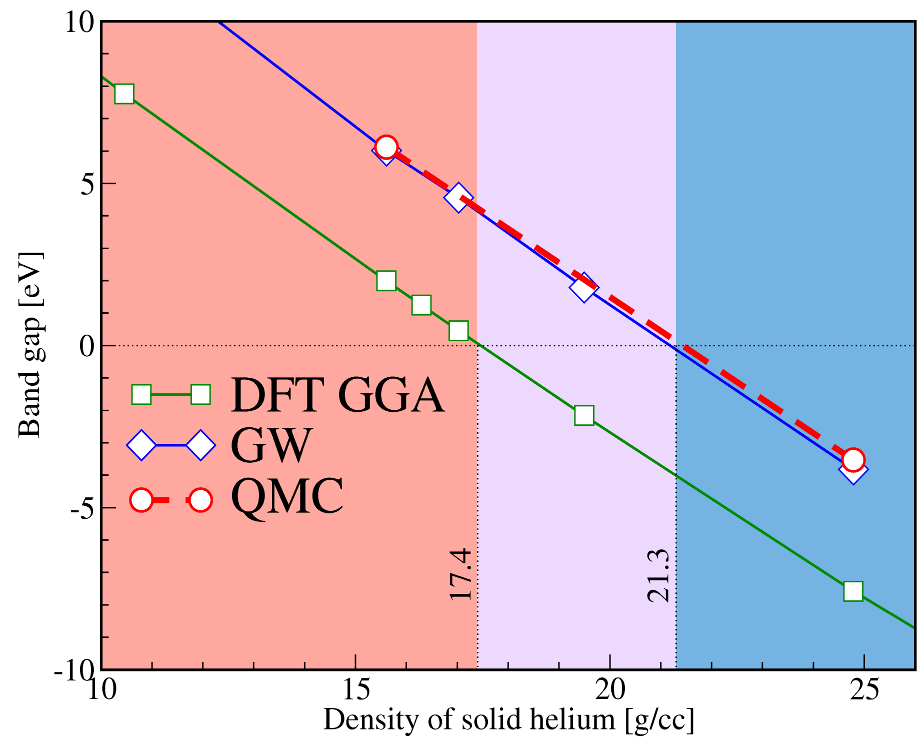
2) Phase Transitions in Silica Quartz

3) Fundamental high pressure scale for cubic boron nitride

QMC Calculation of the Metallization of Solid Helium under Pressure

Method comparison

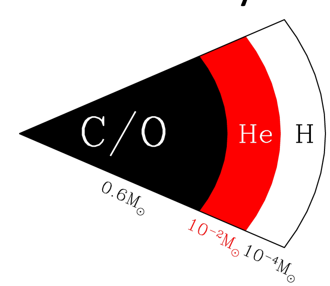
- QMC and GW: agreement
- GGA:
  - ×Underestimates gap by 4eV
  - ×40% difference in pressure
  - ×20% difference in density



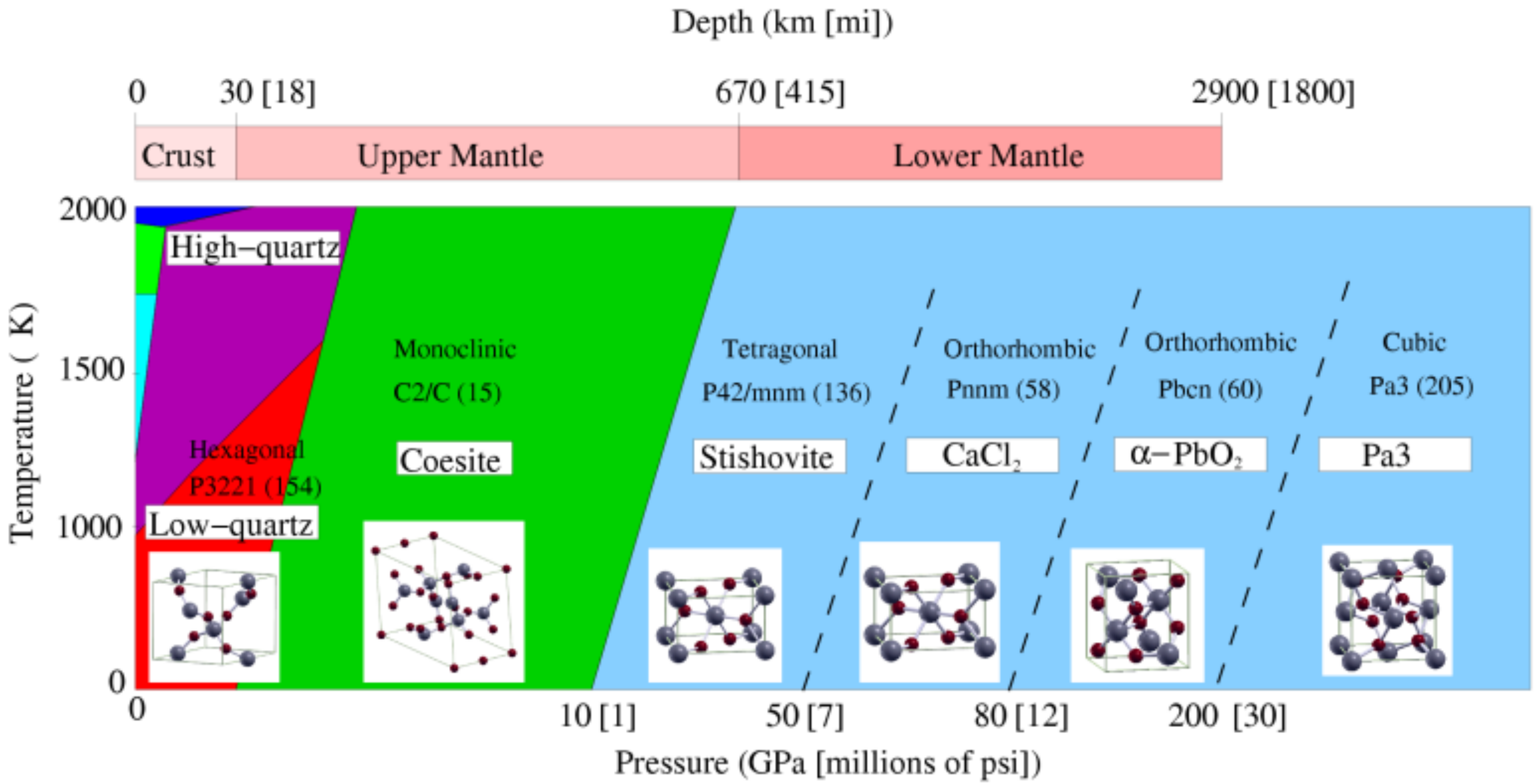
→QMC done with Casino code (Cambridge).

Solid helium metallizes at extreme pressure of 25.7 TPa. This transition is important for the heat transfer in hydrogen-poor white dwarfs.
Khairallah & Militzer, *Phys. Rev. Lett.* **101** (2008) 106407

White dwarf layers:



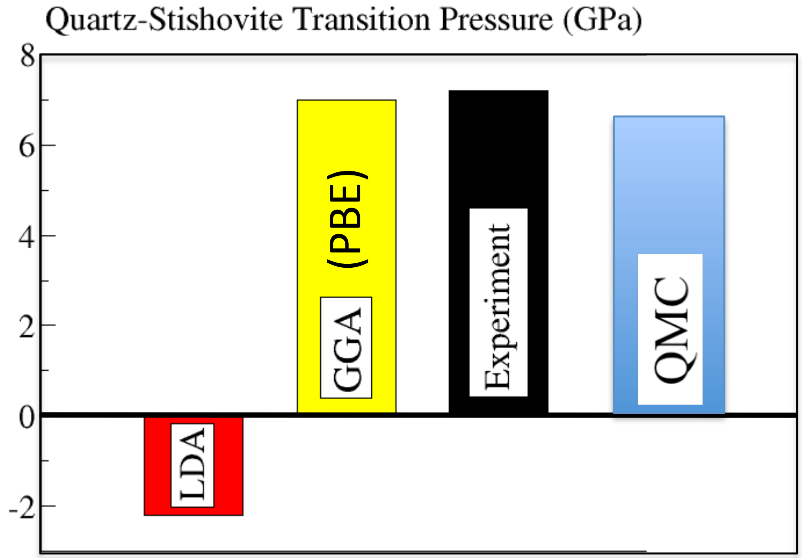
Phase Diagram of Silica SiO_2



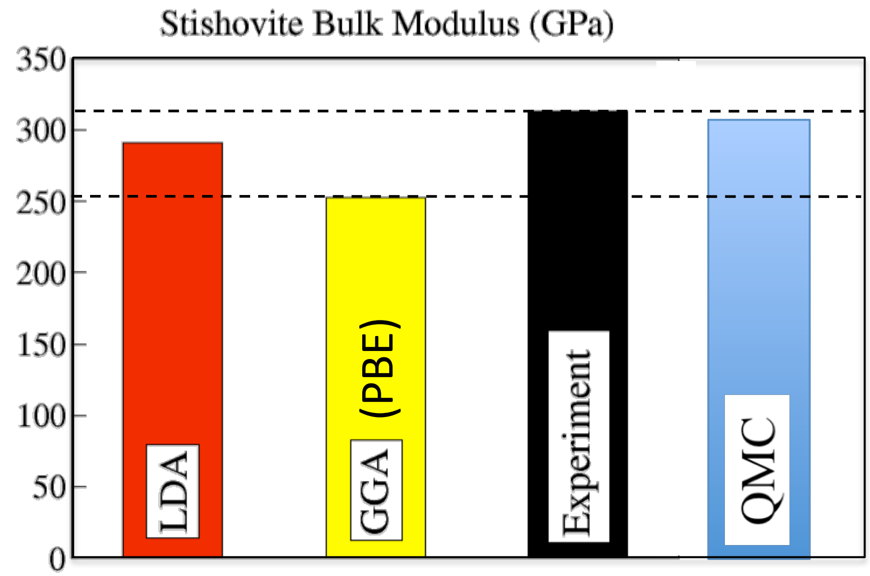
1) Quartz and Coesite are 4-fold coordinated
2) Stishovite and post-stishovite phases are 6-fold coordinated
3) Stishovite undergoes a ferroelastic transition (2nd order) to $CaCl_2$
4) α-PbO_2 is the last structural change before reaching core-mantle boundary

The Choice between Two Imperfect Functionals:

LDA predicts the wrong ground-state structure (stishovite instead of quartz)



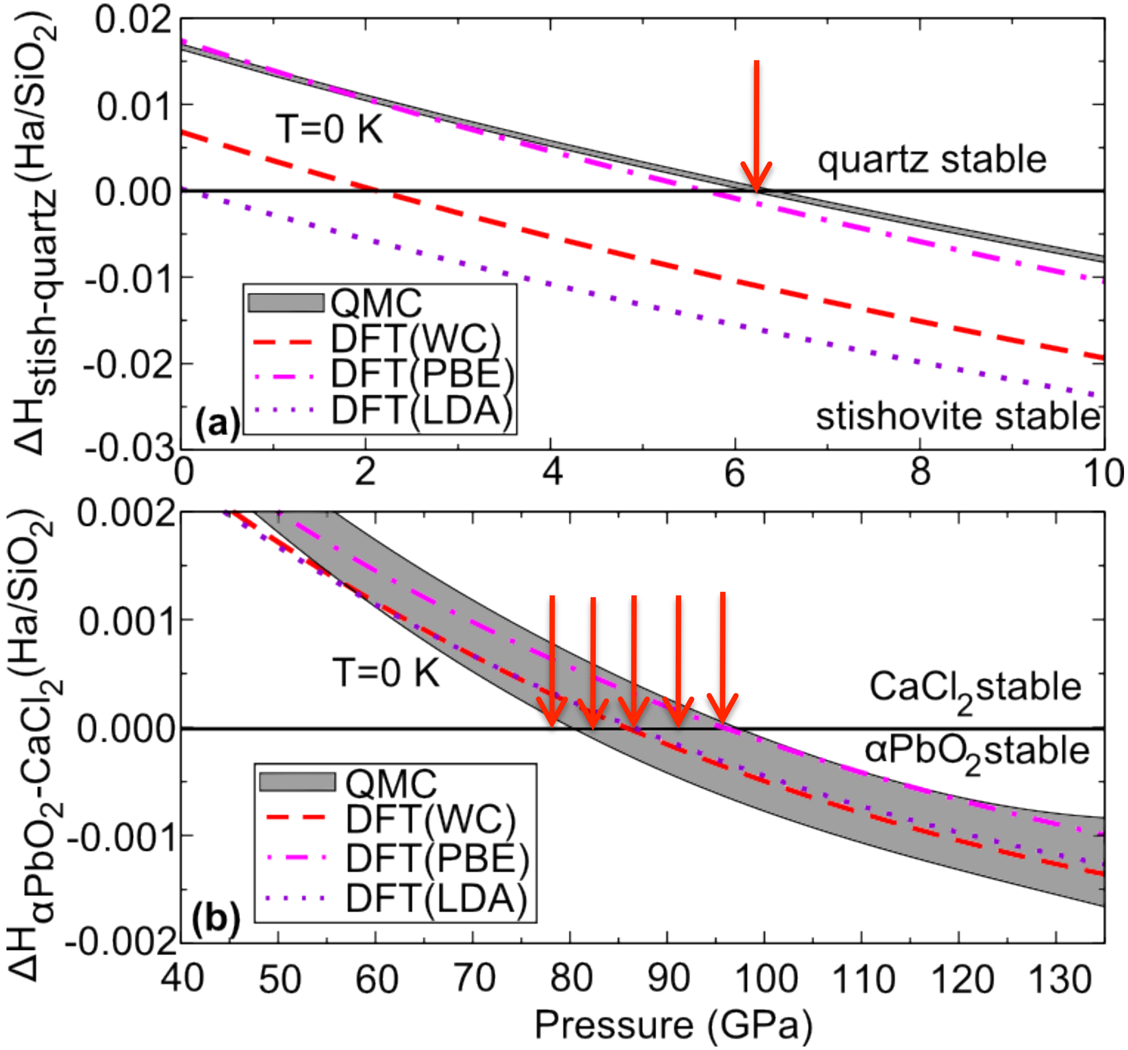
GGA predicts a bulk modulus that is 20% too low



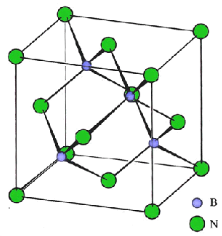
- LDA tends to predict structural properties of given phases better than GGA (lattice and elastic constants)
- LDA fails to predict the quartz-stishovite transition; GGA gets it correct.
- Why? possibly because 6-fold coordinated stishovite has more homogeneous charge density than 4-fold coordinated quartz and coesite. GGA is able to accomodate, but LDA is not. (However, LDA does better than GGA for the quartz-coesite transition)
- DFT functionals can be unreliable; there is no functional which can provide exact results
- QMC explicitly computed the exchange and correlation, offering much better accuracy and reliability.

- John Wilkins' group works on interstitial defects in silicon, silica, and magnesium silicate calculations with QMC.

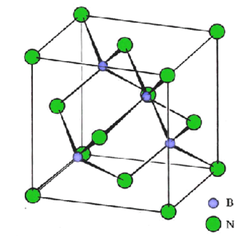
QMC and DFT Predictions for the Transition Pressure Enthalpy Differences vs Pressure



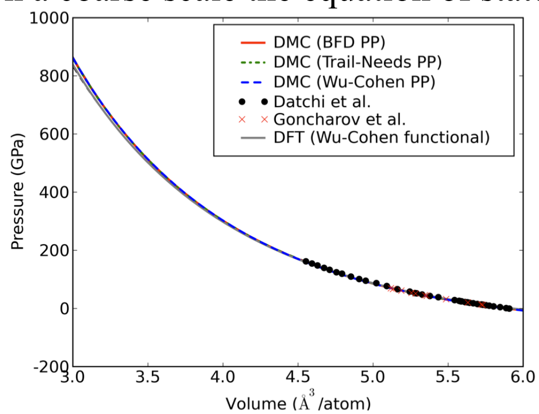
K. Driver *et al.* submitted to *Proc. Nat. Acad. Sci. (2009)*



First All-Electron QMC Calculations performed



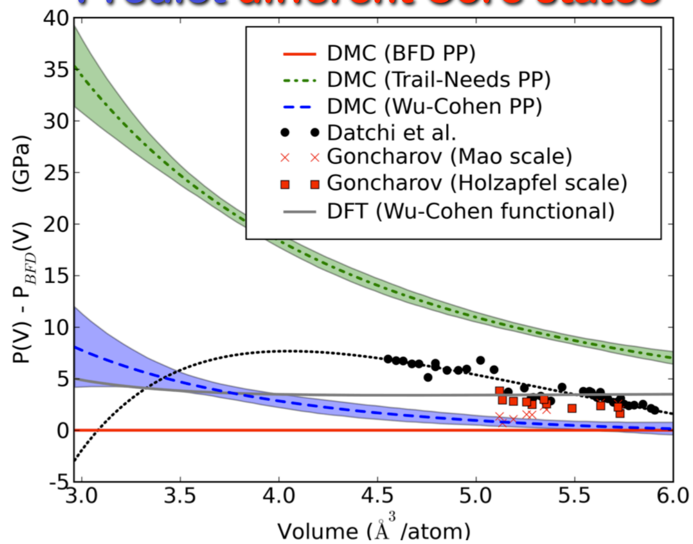
On a coarse scale the equation of state looks fine



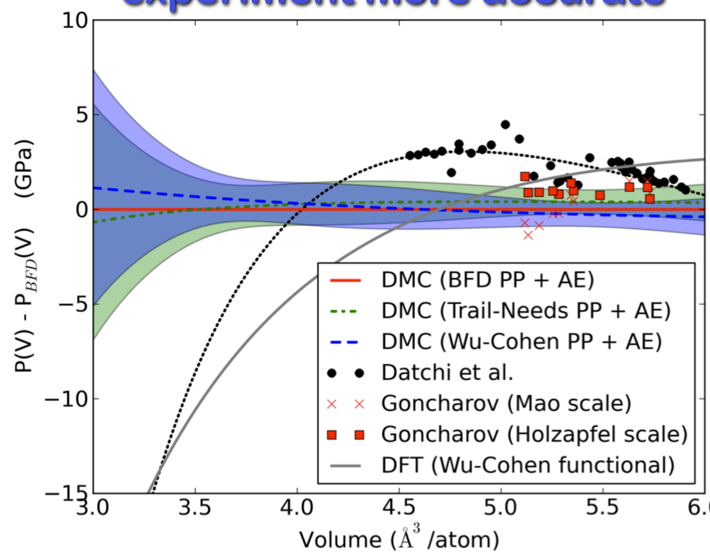
- The goal: A new pressure scale for diamond anvil experiments
- Calibrate using highly accurate simulations rather than experiments.
- First all electron QMC calculations for solids heavier than H and He.
- The pseudopotential approximation avoided.
- Shown that Goncharov's experiments are more accurate.

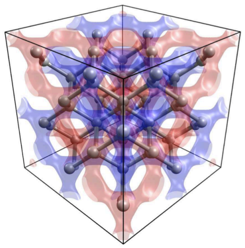
Ken Esler *et al.* submitted to *Phys. Rev. Lett. (2009)*

The Problem: Different DFT Functionals Predict different Core states

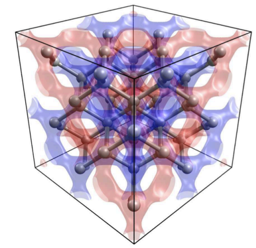


Final Solution: All electron QMC results predict Goncharov's experiment more accurate

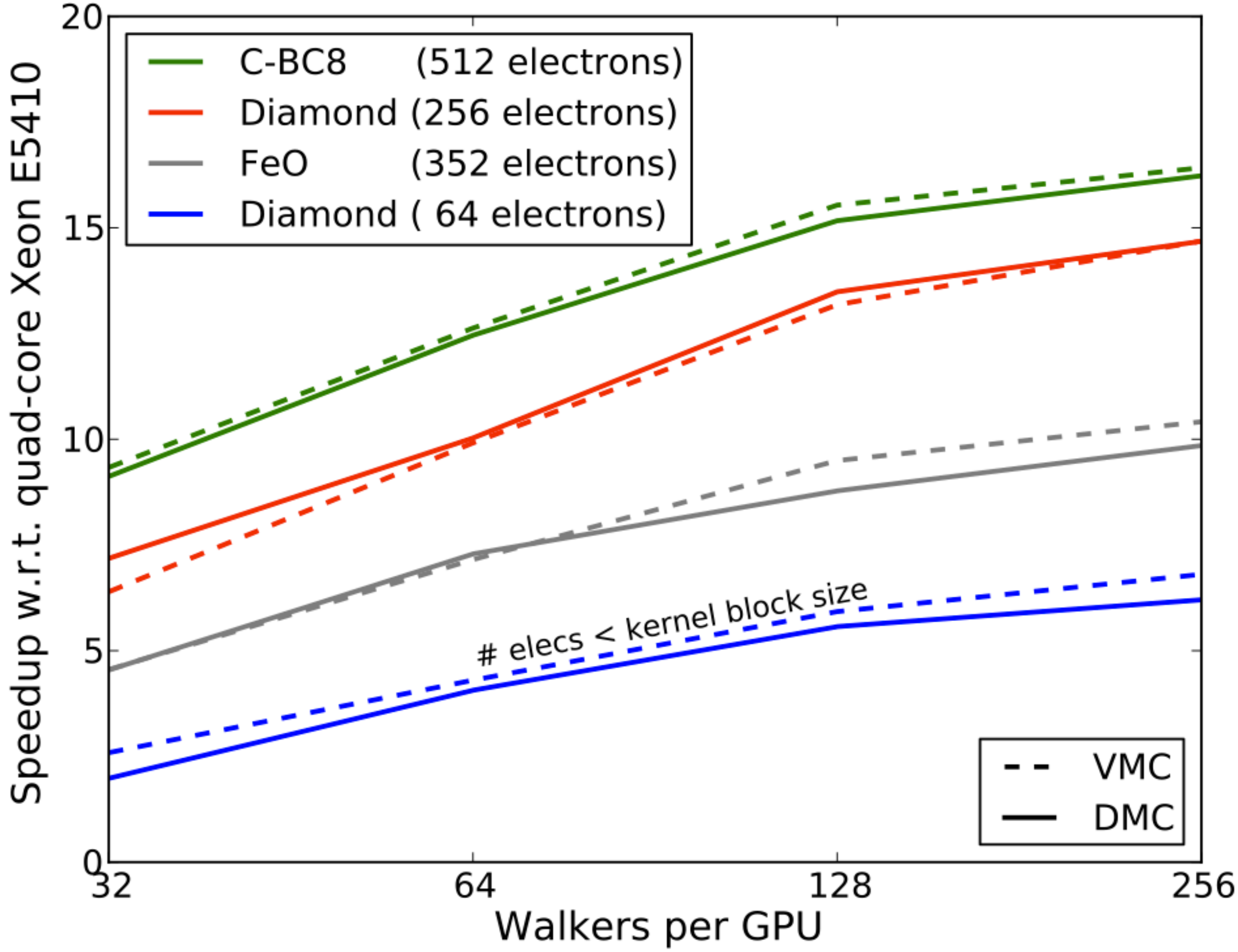


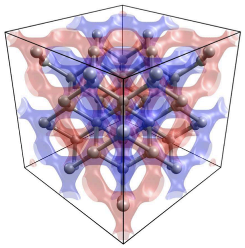


Fabulous 10…15x Speed-Up of QMC on GPU (NVIDIA-CUDA)



Relative to 4 threads





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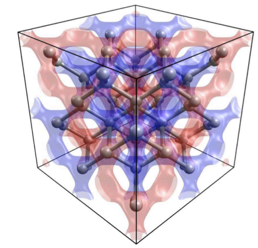

Speed up is a result of new way to parallelize the QMC algorithm (Esler, Kim & Ceperley at UIUC):

Standard way to distribute work among ***CPUs*** using OpenMP/MPI:

```
Loop over MC generation
    Loop of walkers on many CPUs
        Loop over particles
            MC move
            Reweight + branch
            …
        end
    end
end
```

New way to distribute work among ***GPUs***

```
Loop over MC generation
    Loop of particles
        Loop over walkers 4096+ threads per GPU
            MC move
        end
    end
    Loop of particles
        Loop over walkers 4096+ threads per GPU
            Reweight + branch
        end
    end
    …
end
```

Single precision is also used whenever possible.