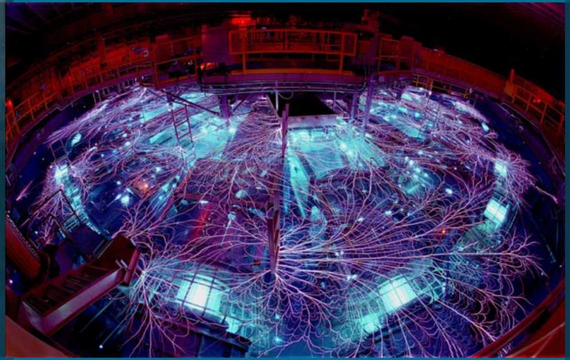
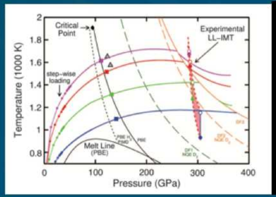
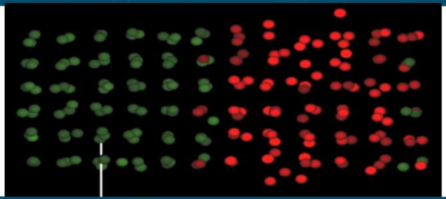
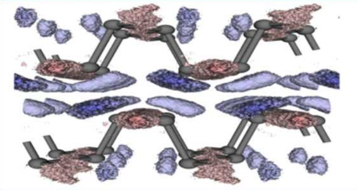
SAND2018-7880C

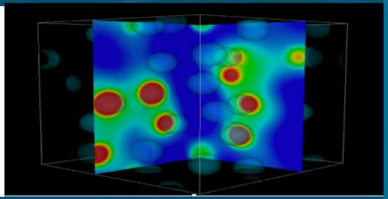
Advances in QMC for high pressure research











PRESENTED BY

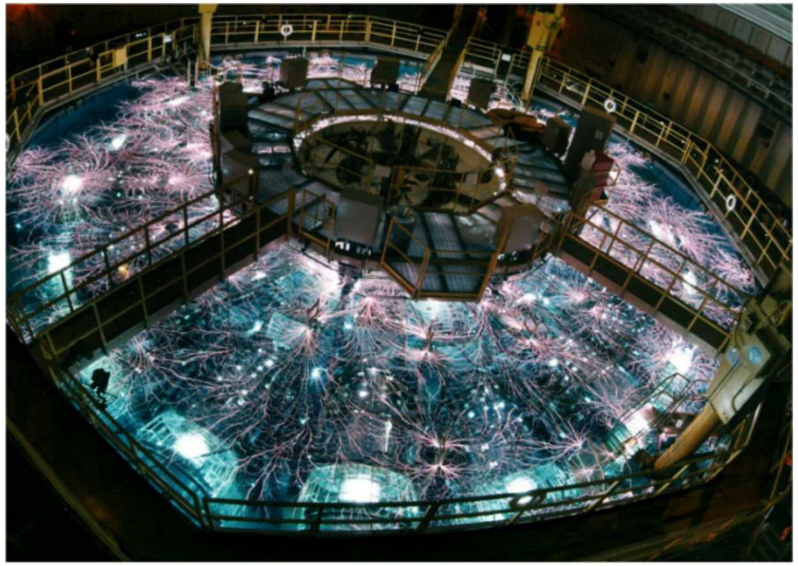
Luke Shulenburger

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

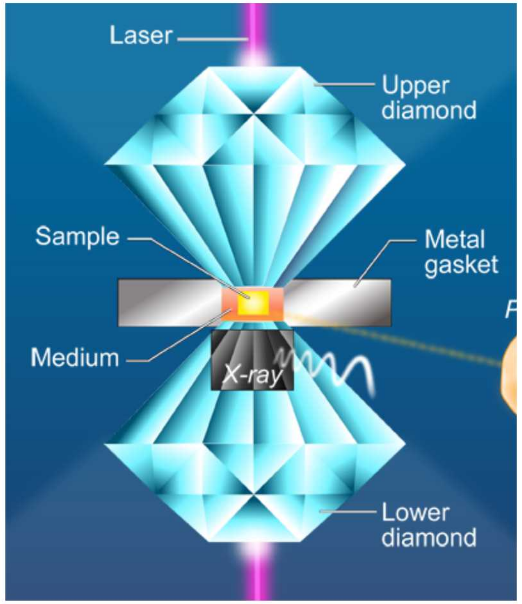
Acknowledgements

- CPSFM
- Thomas Mattsson
- Carlo Pierleoni
- David Ceperley
- Ronald Cohen
- Raymond Clay III
- Joshua Townsend

Challenges of reaching high pressure require compromises



- Uniformity of state
- Small samples, Short times or both
- Diagnostic access



Quantum calculations offer a flexible alternative

- The equations governing the properties of any material under **any** conditions are known

$$\hat{H}\Psi(r_1 \ldots r_N) = E\Psi(r_1 \ldots r_N)$$

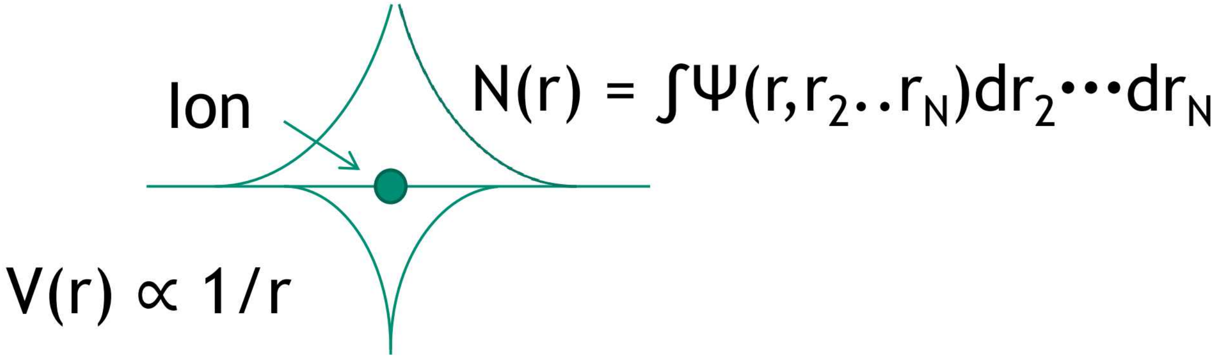
$$\hat{H} = -\sum_i \frac{\nabla_i^2}{2m} + \frac{1}{2}\sum_{i \neq j} \frac{e^2}{\left|\vec{r}_i - \vec{r}_j\right|} + \sum_{i,I} \frac{Z_I e^2}{\left|\vec{R}_I - \vec{r}_i\right|}$$

- Just need to solve the 3N dimensional partial differential equations
- Approximations are necessary for real materials

DFT – The Most Common Approximation

Three insights underpin the development of the most commonly used theory

- Physical Insight

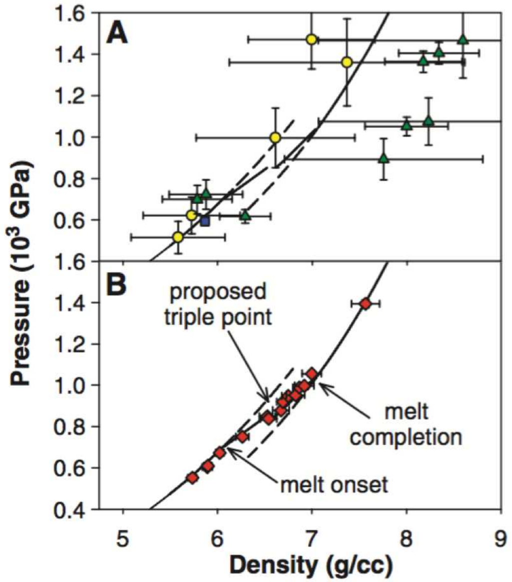


  - Wavefunction is not an observable but the density is
  - Replace the 3N dimensional wavefunction with the 3 dimensional density
- Can approximate kinetic energy and develop a sensible density by solving for noninteracting electrons in an effective potential
- A reasonable approximation is to make the effective potential a simple function of the density

Density Functional Theory is a very successful technique

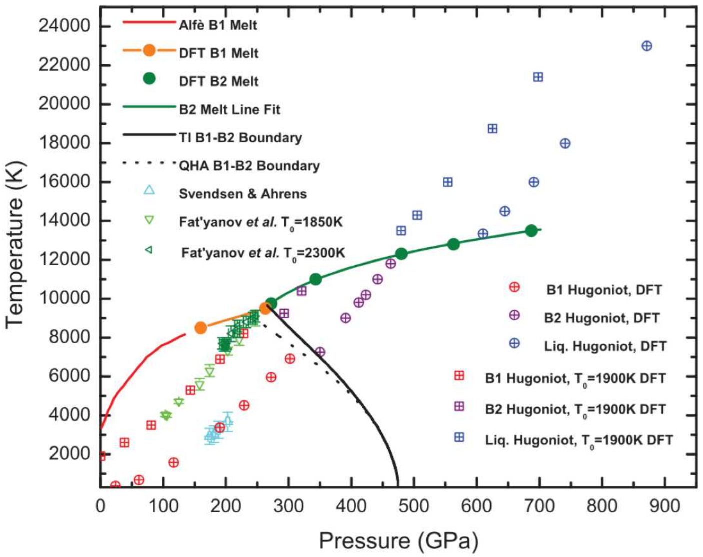
Careful DFT / QMD calculations can complement experiment by providing additional information

Shock melting of diamond



Knudson, Desjarlais and Dolan, Science **322**, 1823 (2008)

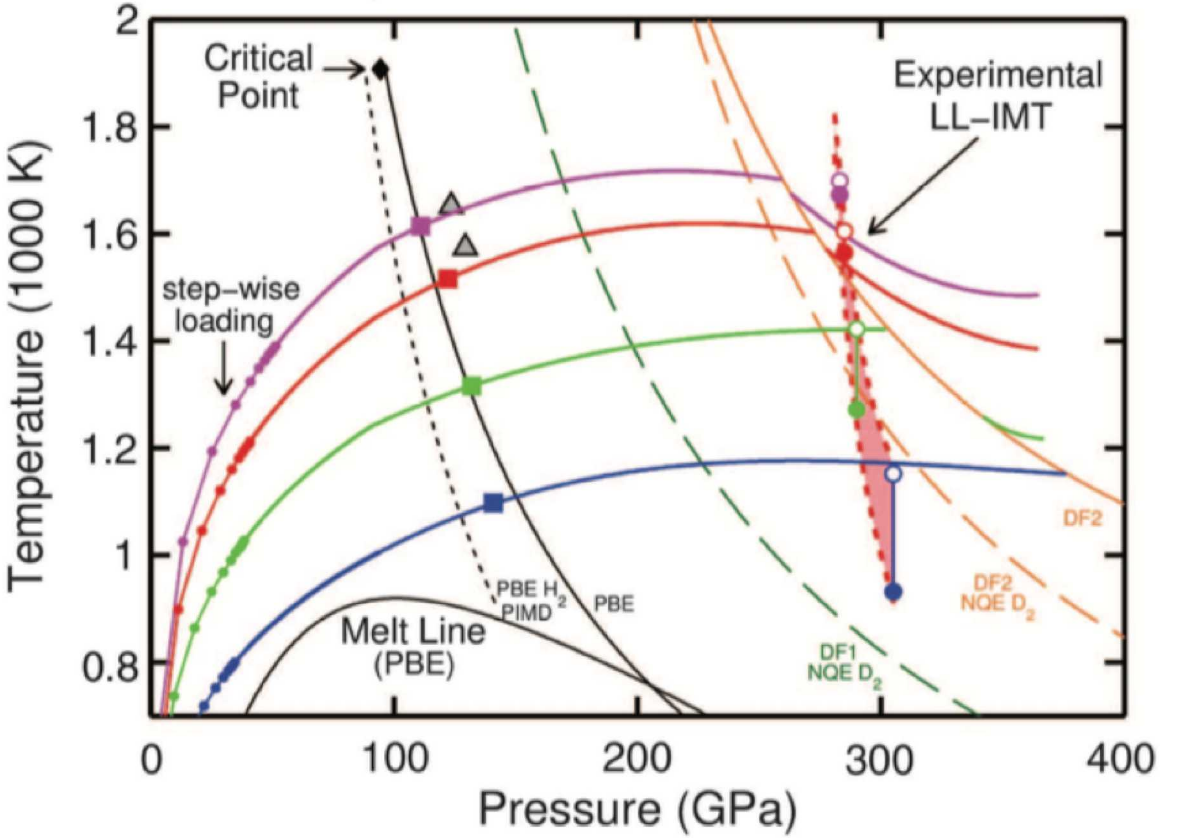
Phase diagram of MgO



Root, LNS, Lemke, Dolan, Mattsson and Desjarlais, PRL **115**, 198501 (2015)

DFT approximations are not always small

- Deuterium liquid-liquid phase transition
- DFT predictions of pressure vary widely between approximations
  - Impossible to determine a priori which one is correct
  - Approximations are notoriously difficult to improve
- Particularly troubling given complexity of experimental analysis
- Can we do better?



Knudson, Desjarlais, Becker, Lemke, Cochrane, Savage, Bliss, Mattsson and Redmer, Science **348**, 1455 (2015)

Quantum Monte Carlo Calculations offer another possibility

- Recast Schrodinger equation as an integral problem in 3N dimensions

$$< \hat{H} >= \frac{\int \Psi^*(\mathbf{R})\hat{H}(\mathbf{R})\Psi(\mathbf{R})d\mathbf{R}}{\int \Psi^*(\mathbf{R})\Psi(\mathbf{R})d\mathbf{R}}$$

- Massive parallelism available, each point can be calculated independently
- Variational principle lets you know when your approximation is improving
- Poor scaling if nontrivial trial wavefunction
  - 3 dimensions per electron
  - 20 points in each direction
  - $20^9 \approx$ 512 billion points for 3 electrons
    - 3.8 TB just to store!
- Stochastic Methods scale much better for multidimensional integrals
- Effort for constant error scales as 1/√N regardless of dimensionality

Taking the next step - Diffusion Monte Carlo (DMC)

- Project wave function in imaginary time

$$\left|\psi(\tau+\delta\tau)\right\rangle = e^{-\hat{H}\delta\tau}\left|\psi(\tau)\right\rangle = \sum_{i=0}^{\infty} c_i e^{-\varepsilon_i\delta\tau}\left|\phi_i\right\rangle$$

- Recast projection in integral form

$$\left|\psi(\mathbf{R}',\tau+\delta\tau)\right\rangle = \int d\mathbf{R}G(\mathbf{R}',\mathbf{R},\tau)\left|\psi(\mathbf{R},\tau)\right\rangle$$

where

- Observables are

$$G(\mathbf{R}',\mathbf{R},\tau) = \left\langle\mathbf{R}'\right|e^{-\tau(\hat{H}-E_T)}\left|\mathbf{R}\right\rangle$$

- For electronic structure, the kinetic term in the Hamiltonian makes this look like a diffusion equation (in 3N dimensions). Other terms become sources and sinks

$$\left\langle\psi_T\right|O\left|\psi_0\right\rangle = \frac{\int \Psi_T(\mathbf{R})\Psi_0(\mathbf{R})\frac{O(\mathbf{R})\Psi_T(\mathbf{R})}{\Psi_T(\mathbf{R})}d\mathbf{R}}{\int \Psi_T(\mathbf{R})\Psi_0(\mathbf{R})d\mathbf{R}}$$

Why are QMC calculations not exact?

- Monte Carlo Samples a probability distribution
  - Electrons are Fermions! (wavefunction is not >0 everywhere)
- Use guiding (trial) wavefunction, Ψ, for importance sampling and for fixed node approximation
- Ψ is not the exact many-body wavefunction
  - Built using single particle orbitals calculated externally
  - Energy only depends on Ψ=0 manifold

How are QMC calculations used for high pressure in practice?

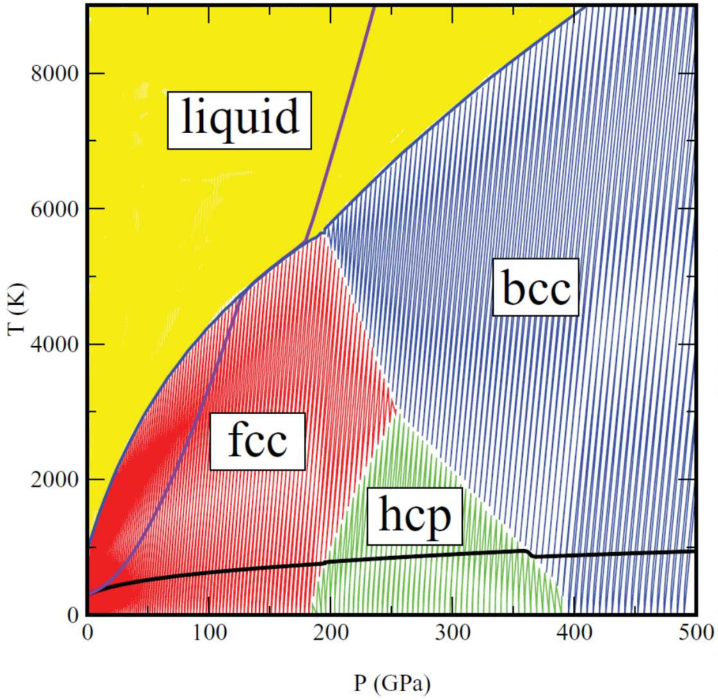
- More expensive, so typically used when DFT is not well trusted or high accuracy is needed
- Example of uncertain Al phase diagram
  - Given a dynamic experiment, how do kinetics influence the perceived phase boundaries?
  - See for example J. Belof's talk from earlier this conference

How are QMC calculations used for high pressure in practice?

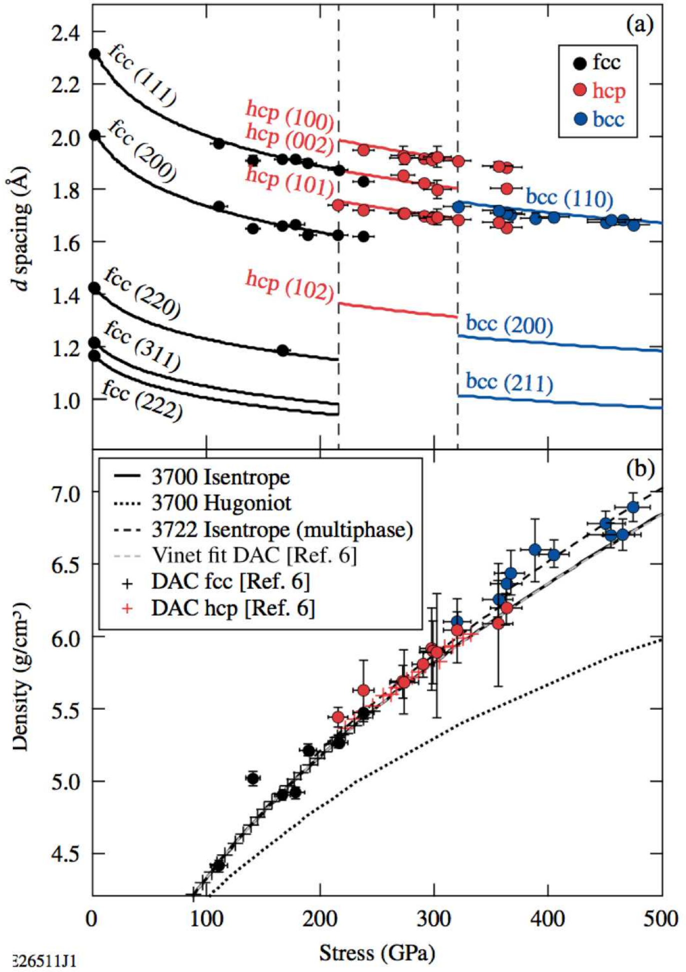
- More expensive, so typically used when DFT is not well trusted or high accuracy is needed
- Example of uncertain Al phase diagram
  - Given a dynamic experiment, how do kinetics influence the perceived phase boundaries?

Sjostrom, Crockett and Rudin,
Phys Rev B **94**, 144101 (2016)

Solid phases primarily treated with DFT – PBE and quasiharmonic or renormalized phonon frequencies

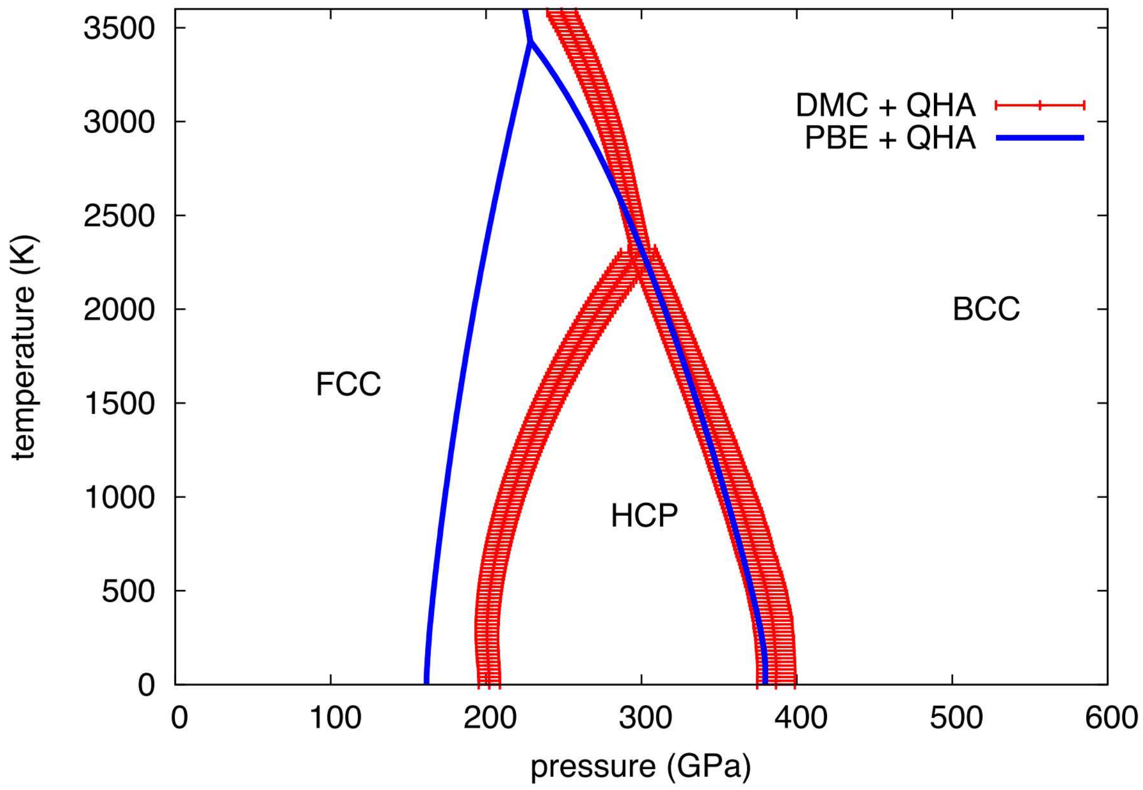


Polsin et al. PRL **119**, 175702 (2017)
DAC with X-ray diffraction



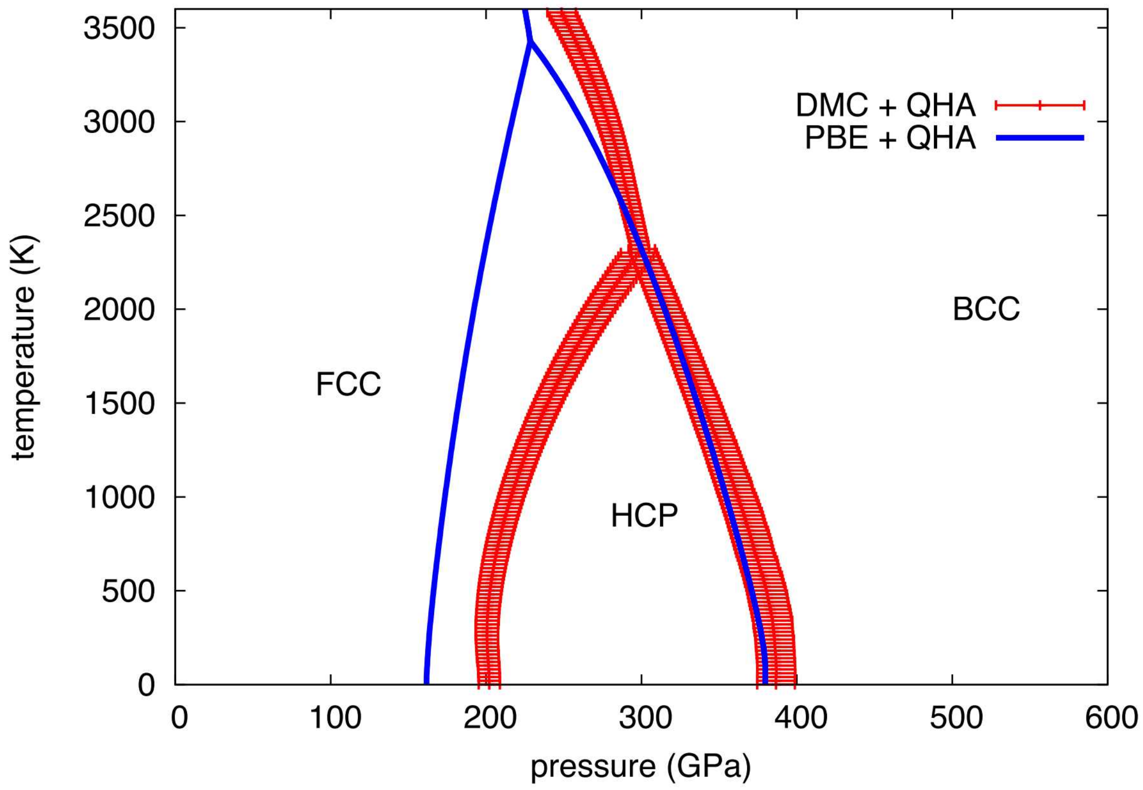
QMC calculations refine the phase diagram

- Use QMC to calculate cold curves of each phase
  - Same treatment of ion-thermal contribution
- Phase boundaries to higher pressures
- Triple point a lower temperature



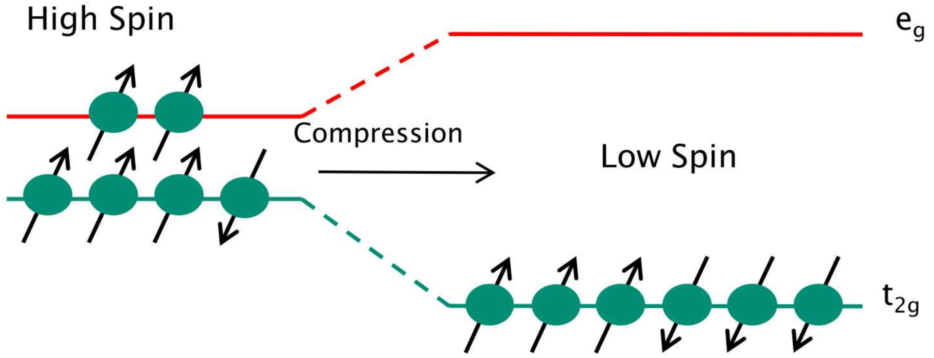
QMC calculations refine the phase diagram

- Use QMC to calculate cold curves of each phase
  - Same treatment of ion-thermal contribution
- Phase boundaries to higher pressures
- Triple point a lower temperature
- Which prediction should we trust?

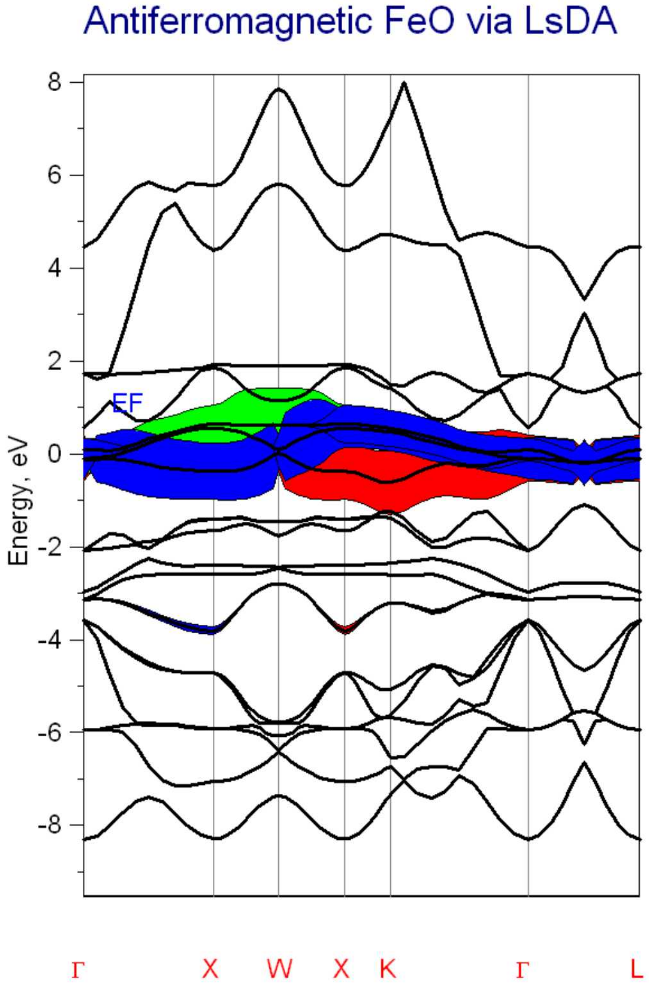


What about a case where DFT is known to have problems?

- Strongly correlated transition metal oxides: FeO
  - Competition between localization and hybridization
  - Iron d-states pose a problem

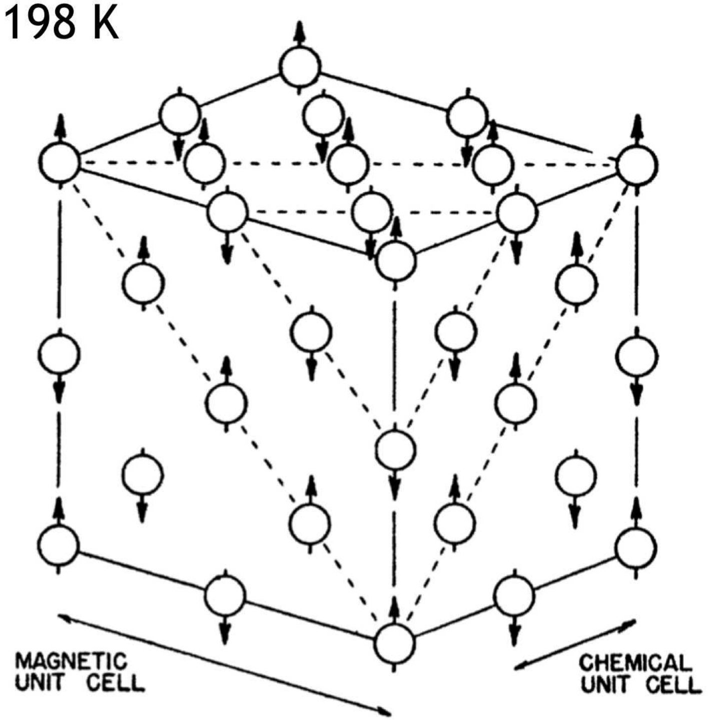


- Standard DFT techniques don't even predict an insulator



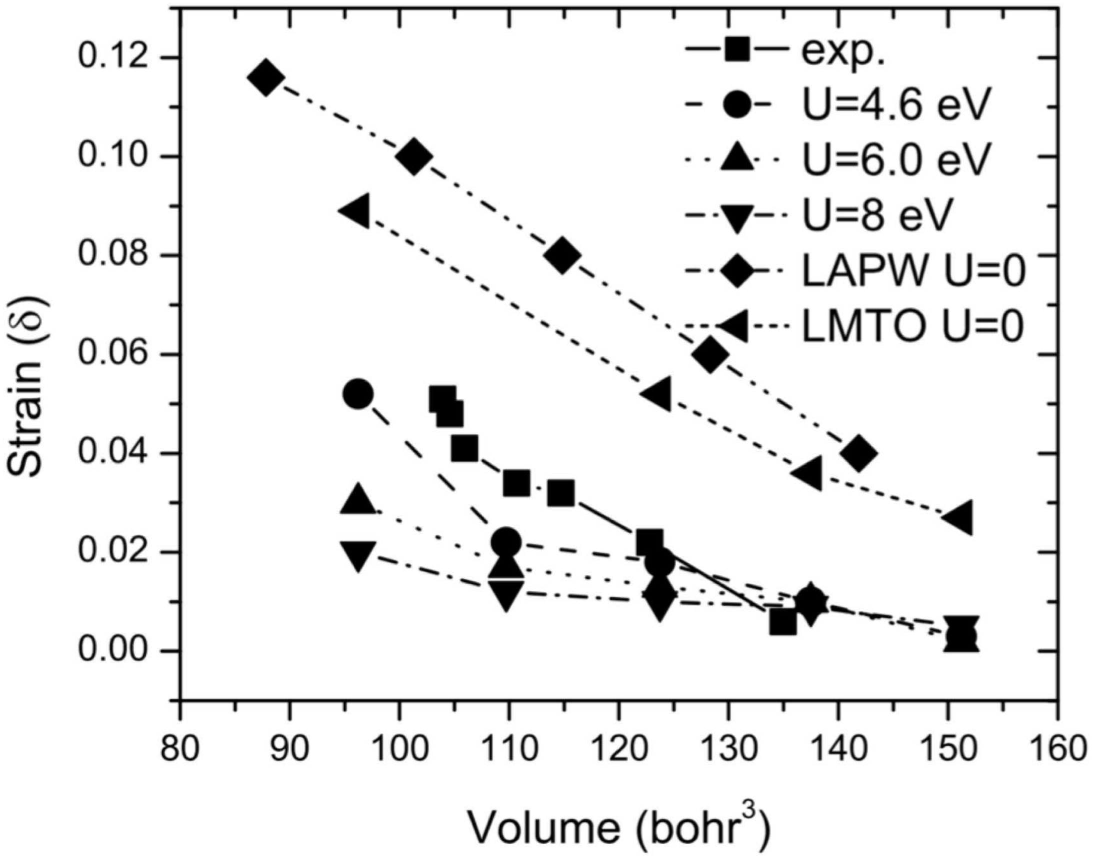
Magnetoelastic coupling in FeO at low temperature

Magnetic ordering causes FeO to distort along 111 direction below 198 K



Schull et al, Physical Review 1951

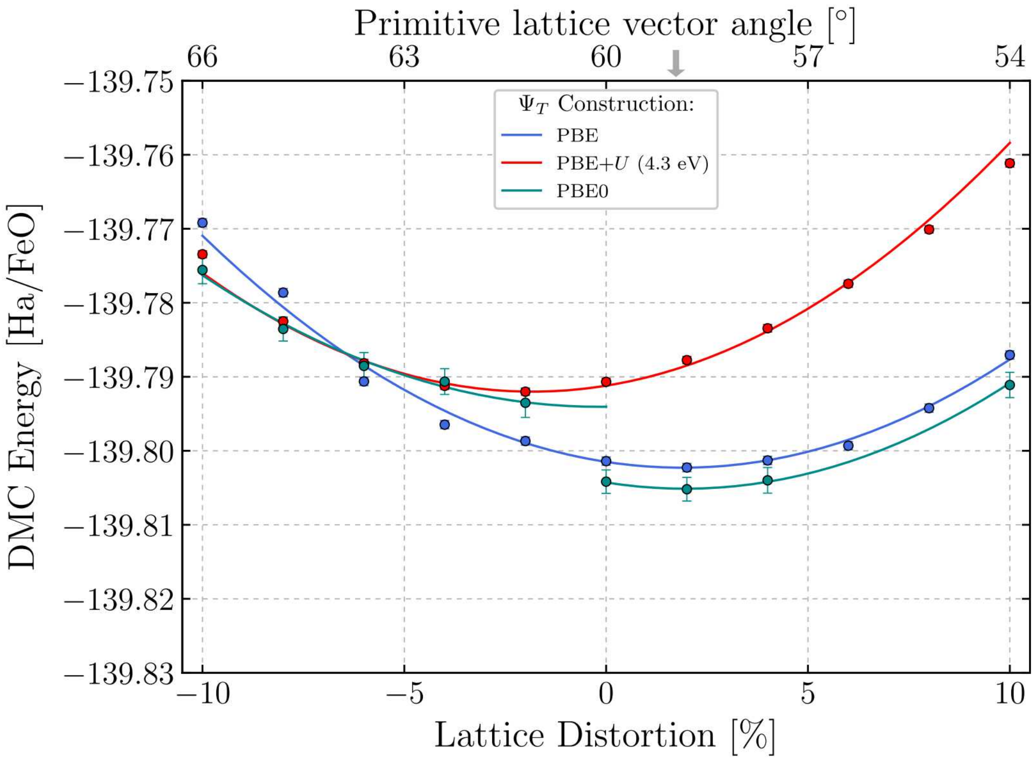
Various DFT treatments have difficulty reproducing experiment because treatment of d-states is crucial



Gramsch et al. 2003

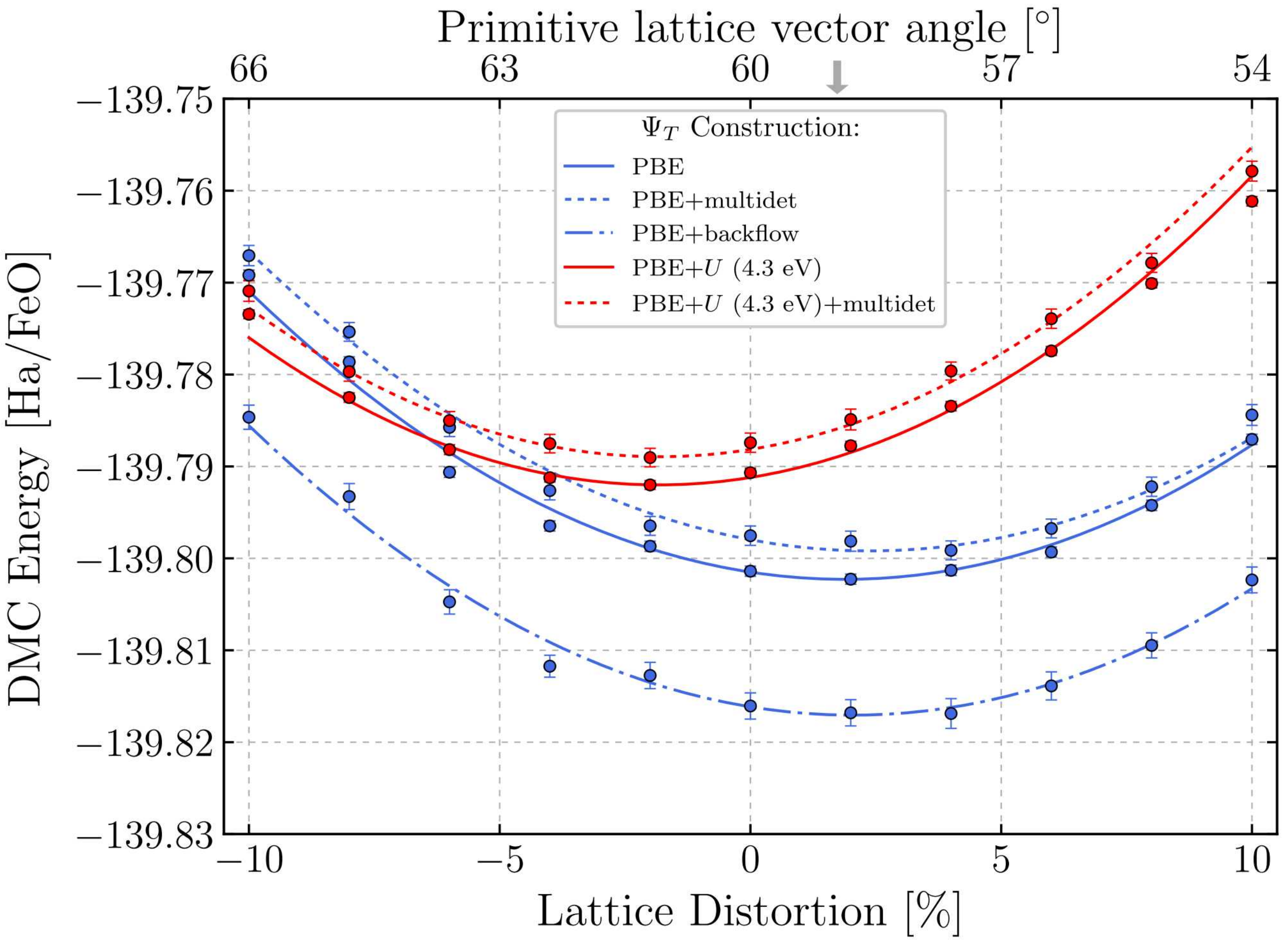
Can QMC do any better?

- To do calculation, need to use trial wavefunction
  - Calculate the energy vs strain using orbitals from DFT type calculations
    - Little effect in weakly correlated material like Al or MgO
  - Strong and uncontrolled approximation for FeO



Introduce flexibility for d-states by optimizing more advanced forms

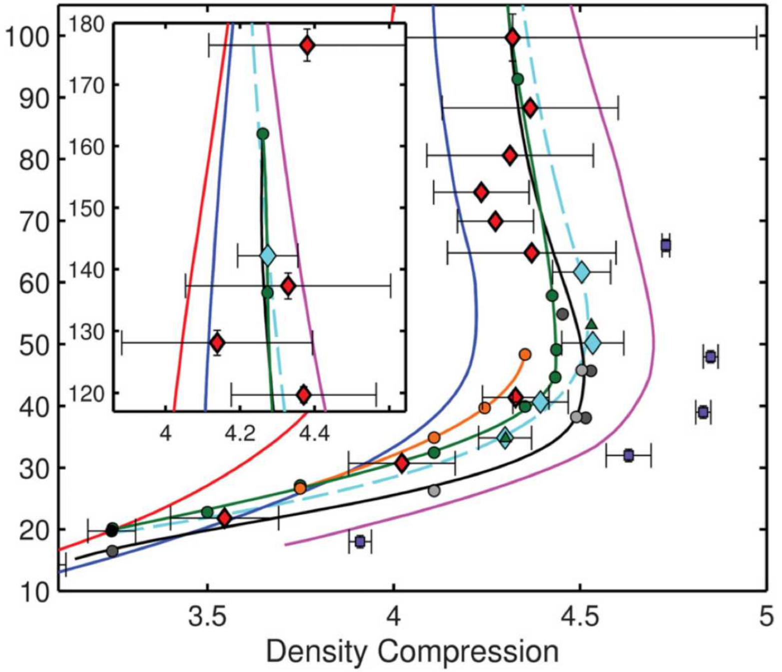
- Backflow or multi-determinants can make inprovements, but the starting point dependence remains



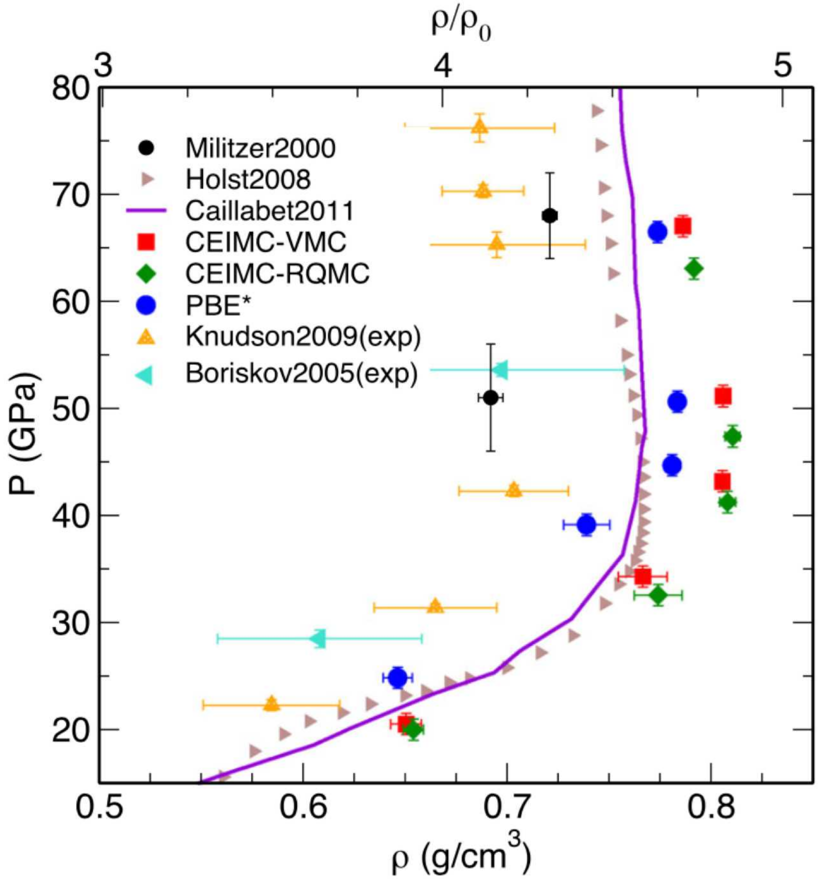
Townsend et al. in preparation

Take a step back and try something simpler – D_2 Hugoniot

- Coupled electron-ion calculation of Hugoniot
- Significantly more compressible than experiment
- This includes non-controversial gas gun experiments



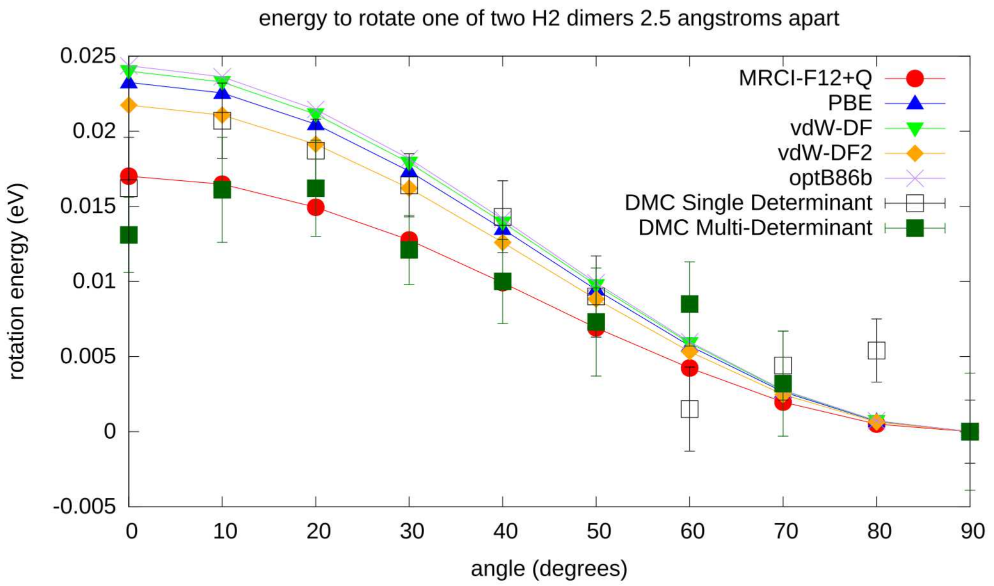
Knudson and Desjarlais, PRL **118**, 035501 (2017)

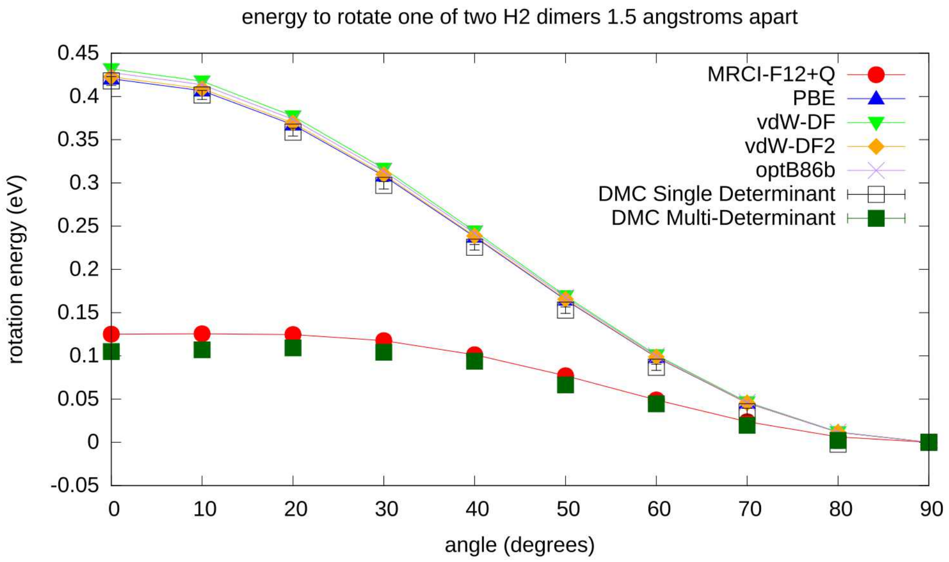


Tubman, Liberatore, Pierleoni, Holzmann and Ceperley, PRL **115**, 045301 (2015)

Why could CEIMC disagree with experiments?

- CEIMC work uses Slater-Jastrow-Backflow Wavefunction
- Such an ansatz does not necessarily capture static correlation correctly
- Ongoing problem to handle this for condensed phases
- Approximation is larger when more highly compressed

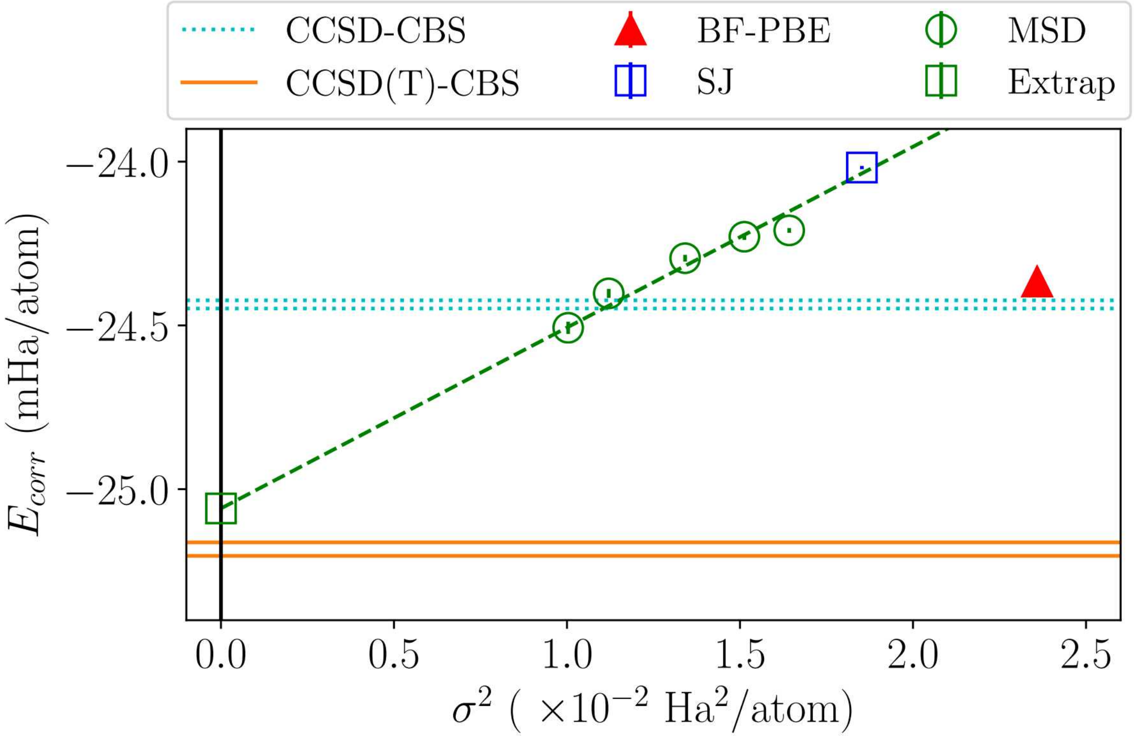




Take the next step for the Hugoniot calculation

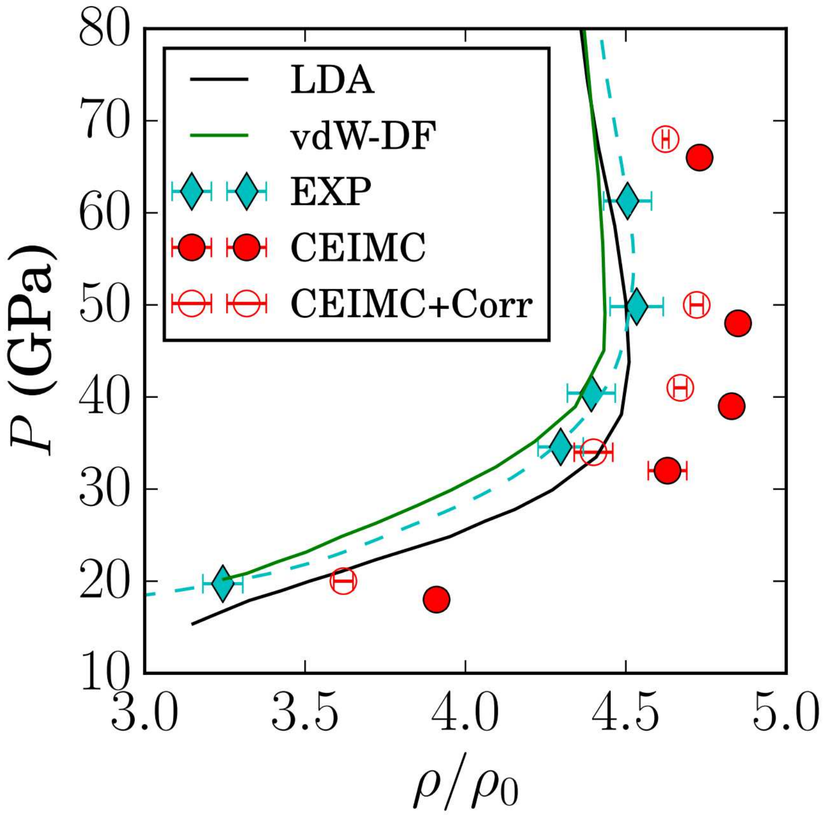
- Apply QMC with various trial wavefunctions to a representative snapshot of the compressed gas
- QMC gives a hint about how accurate the calculation is: Follow the noise!
  - As sampling variance goes down, answer improves
- Carefully constructed classes of trial wavefunctions allow for extrapolation
- Currently only possible for small systems

Energy vs Variance for a small calculation of deuterium



Leverage this to understand effects of errors on the calculated Hugoniot

- Principle problem was QMC errors were small but unbalanced
  - Initial dilute gas was almost exact
  - Shocked state had errors
- DFT errors were much larger, but largely cancelled
- Systematic improvement was much more important (and feasible) than eliminating errors entirely

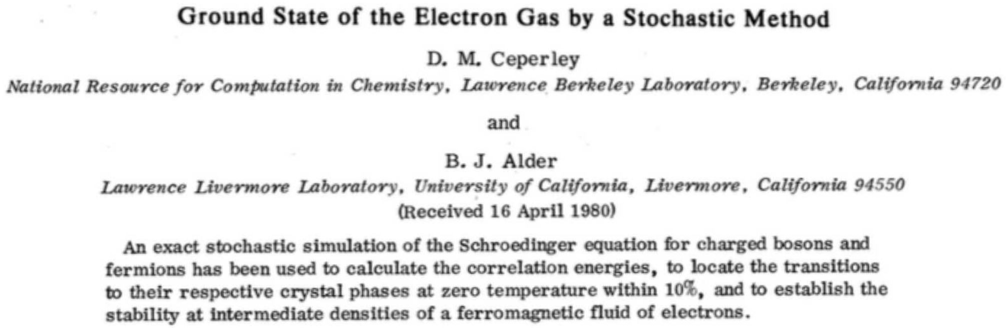


Clay et al. in preparation

QMC with known error bounds is not new

In 1980 Ceperley and Alder used DMC to calculate the energy of the electron gas

Used exponentially scaling version of DMC (released node)



Ground State of the Electron Gas by a Stochastic Method

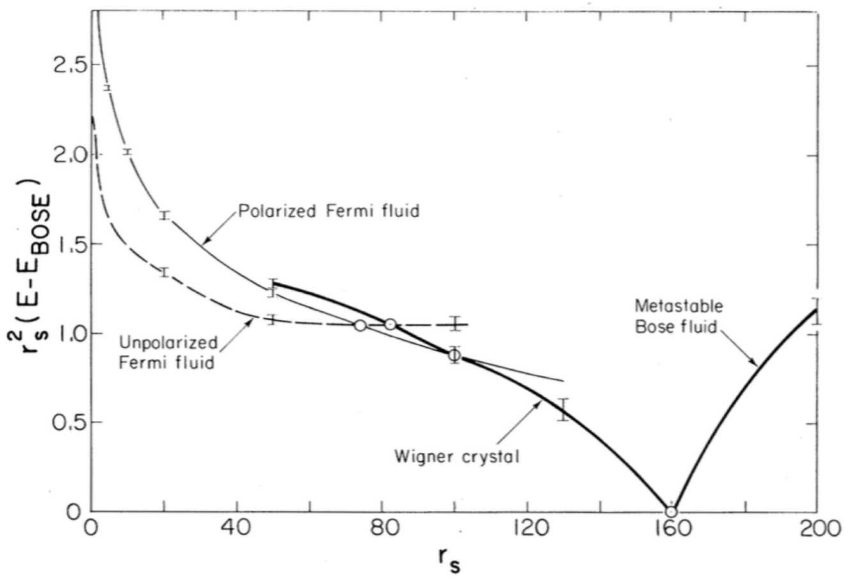
D. M. Ceperley
National Resource for Computation in Chemistry, Lawrence Berkeley Laboratory, Berkeley, California 94720

and

B. J. Alder
Lawrence Livermore Laboratory, University of California, Livermore, California 94550

(Received 16 April 1980)

An exact stochastic simulation of the Schroedinger equation for charged bosons and fermions has been used to calculate the correlation energies, to locate the transitions to their respective crystal phases at zero temperature within 10%, and to establish the stability at intermediate densities of a ferromagnetic fluid of electrons.



QMC can offer a new way of performing calculations at high pressure

- Standard quantum calculation techniques are quite useful, but their accuracy is unknown
  - It is not always clear (even to experts) when calculations will show errors
- QMC has the advantage of performing calculations using the ab initio Hamiltonian
  - This does not always guarantee higher accuracy than DFT
- There are ways to control errors with QMC
  - For example, comparing variance to total energy
  - May allow one to say how accurate their calculations actually are!