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Understanding quantum Monte Carlo applied to Warm Dense Matter

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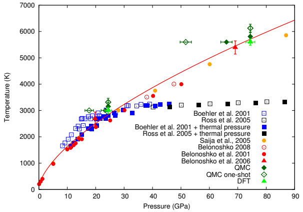

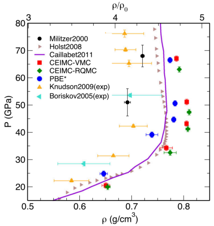

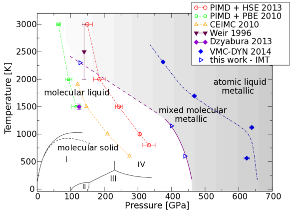

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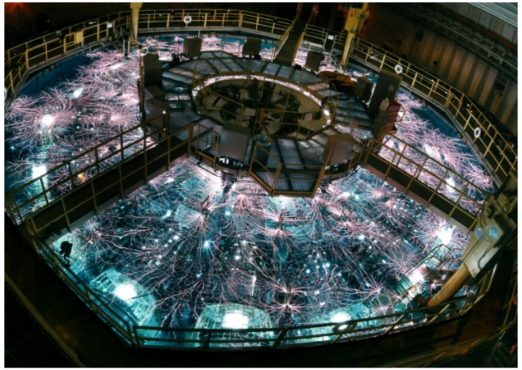
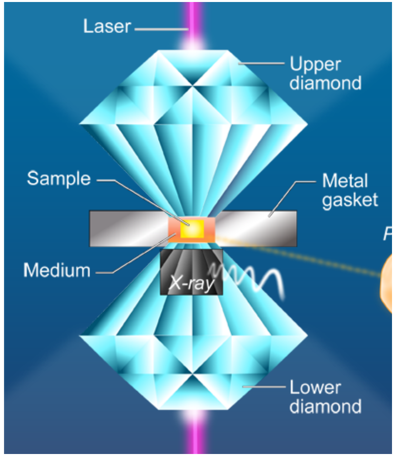
Techniques to probe materials at extreme conditions





Why Quantum Calculations?

- Equations governing the properties of a material under any conditions are known

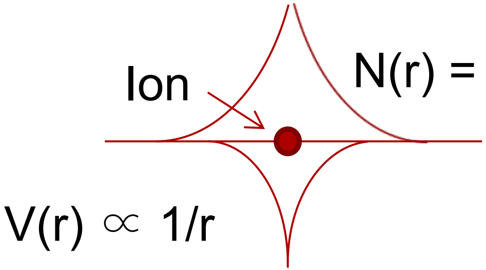
$$\hat{H}\Psi(r_1 \ldots r_N) = E\Psi(r_1 \ldots r_N)$$

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

- 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



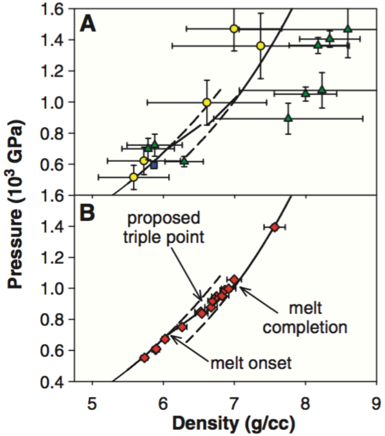
$$N(r) = \int \Psi(r, r_2 .. r_N) dr_2 \cdots dr_N$$

    - Wavefunction is not an observable but the density is
    - Replace the 3N dimensional wavefunction with the 3 dimensional densiy
  - 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

DFT is a very successful technique for studying WDM

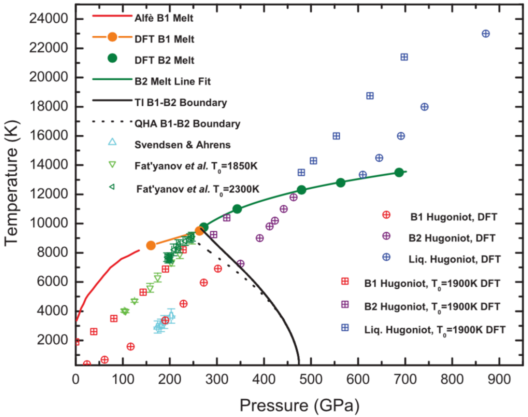
- Careful DFT / QMD calculations can complement experiment by providing additional information
- This is especially powerful when experiments can validate approximations

Shock melting of diamond



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

Phase diagram of MgO

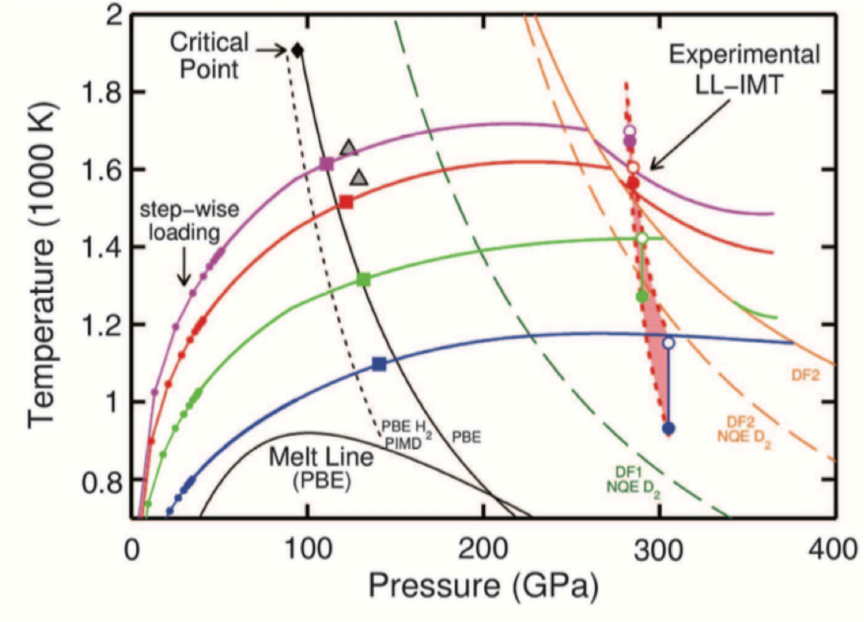


Root, LNS, Lemke, Dolan, Mattsson and Desjarlais, PRL **115**, 198501 (2015)

DFT is not perfect

- Scaling with temperature
  - Memory ~ T^3
  - CPU time ~ $T^{4.5}$
- Approximations are notoriously difficult to improve
- These shortcomings are not just academic!

D_2 liquid-liquid phase transition



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

How to get around the approximations?

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

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

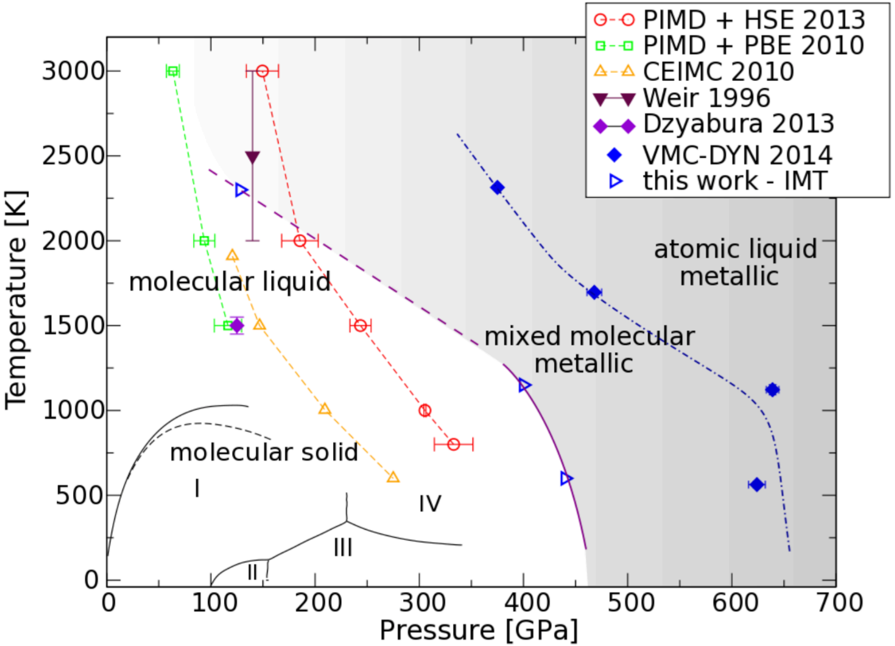
- Massive parallelism available, each point can be calculated independently
- Variational principle lets you know when your approximation is improving
- Poor scaling if nontrivial trial wavefunction
  - 3 dimensions per electron
  - 20 points in each direction
  - $20^9 \approx$ 512 billion points for 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 → VMC

How accurate is VMC?

- How creative can you be in writing down a many body wavefunction?
  - Must be antisymmetric for Fermions – Slater determinants
  - Jastrow factors – Explicitly build in short range correlation
  - Backflow transformation – Feynman ansatz adding in longer range correlation
  - Pairing wavefunctions – For example BCS type pairing of electrons
  - General multideterminant expansions – CI type ansatz, exact but naively scales factorially
- Parameterized forms are optimized using variational principle
  - For small chemical systems, can be exact
  - Accuracy can be uneven when character of system changes

How accurate is VMC?

- Example from literature
- Molecular dissociation of hydrogen
- Langevan dynamics performed using an AGP wavefunction
- Molecular phase is described much better than metallic fluid
- Phase transition is moved to higher pressure



Mazzola and Sorella, PRL **114**, 105701 (2015)

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

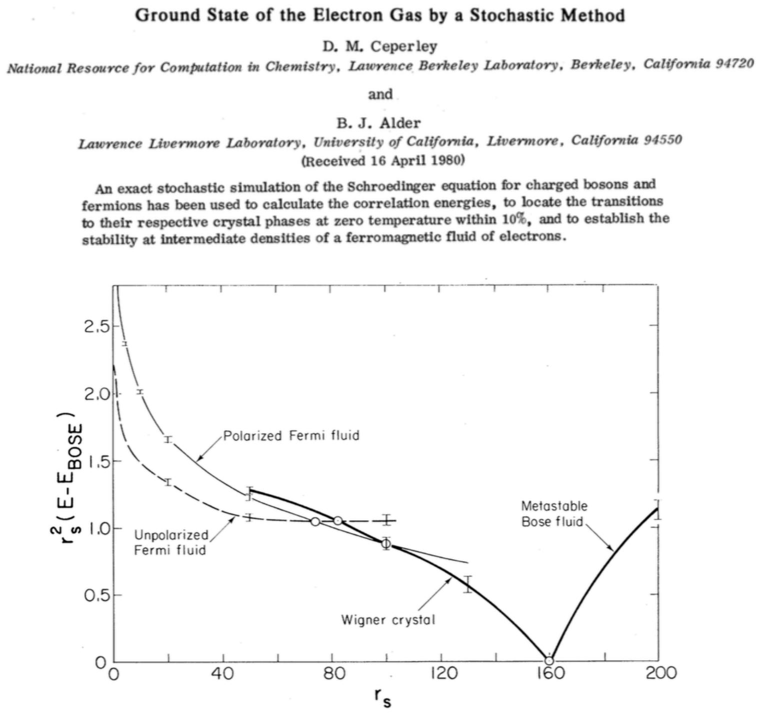
- Observables are

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

- 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

DMC calculations have been important for decades

- In 1980 Ceperley and Alder used DMC to calculate the energy of the electron gas
- Results underpinned the basis for many generations of DFT exchange correlation functionals
- Used exponentially scaling version of DMC
(released node)



Ground State of the Electron Gas by a Stochastic Method

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(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.

What approximations are necessary?

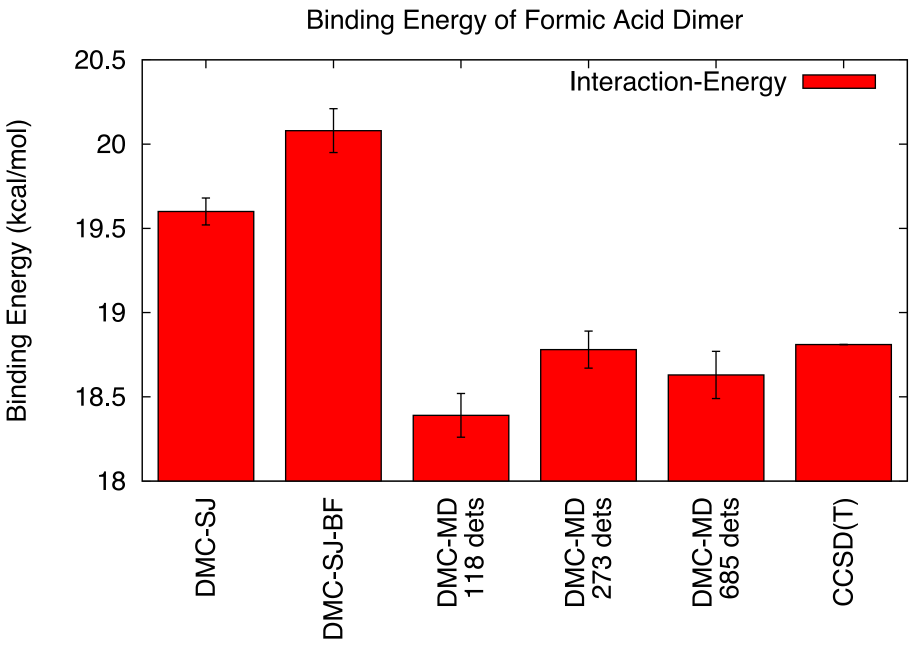
- For Fermions wavefunction is not positive definite
  - Exchange of particles changes sign of wavefunction
  - Statistics of particles is not inherent in Hamiltonian (or propagator)
    - Diffusion will proceed to Bosonic ground state
    - If properties are calculated for antisymmetric state, signal to noise -> 0
- Make the ”fixed node approximation”
  - Assume that trial wavefunction has the same nodes (zeroes) as the exact one
  - Don’t allow moves that change the sign of the trial wavefunction
  - This is variational in the nodal surface

What approximations are necessary?

- Method is also expensive (but very parallel…)
  - Small supercells are required → finite size effects
  - Ions tend to be over-structured when supercells are small
  - Electrons suffer similar problem, but sophisticated schemes exist to correct this
- Electron temperature is zero
  - Minimal condition is that temperature is much less than T_F
  - Better if $T << E_{gap}$
- Core valence interaction can be difficult
  - Poor scaling with ionic charge
  - Replace chemically inert electrons with effective potential
  - Forms for potential can introduce approximation

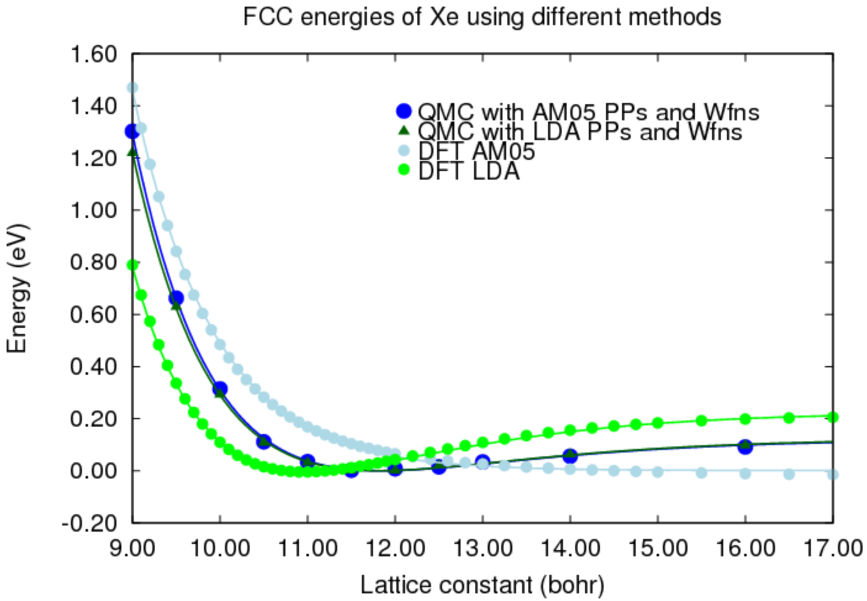
Where does this work well?

- Best case is where approximations can be tested



Case study for melting of Xe under pressure

- Validate approximations for known phase
- Compare E(V) curve of FCC xenon to experiment
  - Starting from two different points results in very similar answers
  - Both answers compare well to experiment



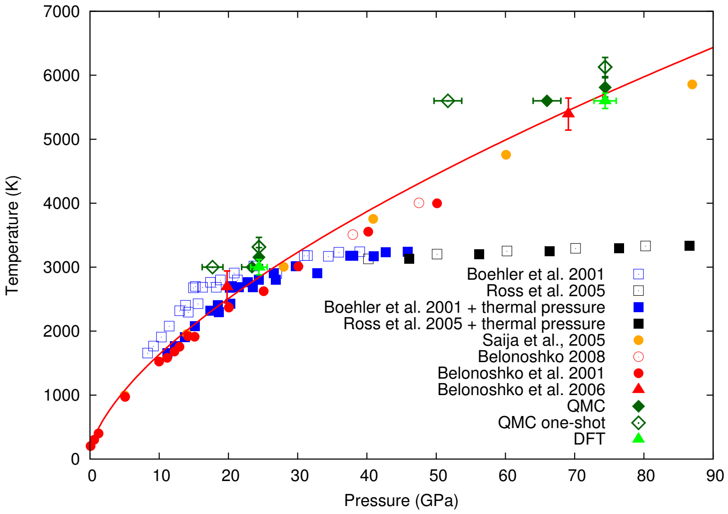
Upscale limited calculations using thermodynamic integration

- Thermodynamic integration also allows relation of free energies from one interaction to another
- Use abstract parameter to tune from DFT interaction to DMC

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

- Terms on right assume that difference in dynamics between DFT and DMC is small (fluctuation terms above are small)

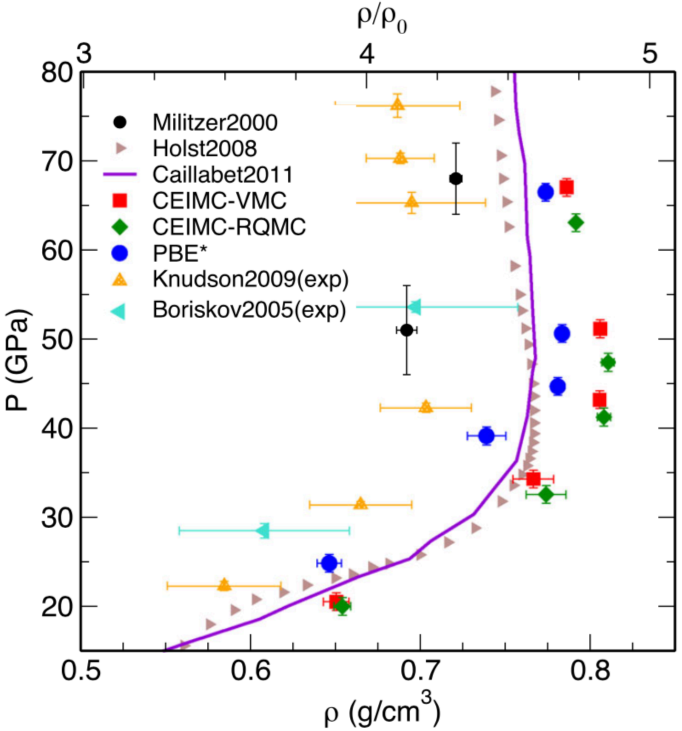
Melting of Xe under pressure



LNS, Desjarlais and Mattsson, PRB, 90, 140104(R) (2014)

What about applying this to hydrogen

- Biggest question revolves around dissociation of molecules under P and T
- Coupled electron-ion Monte Carlo
  - Sample Boltzmann distribution for ions using MC based energy differences
  - Apply a variety of corrections to account for electronic temperature / finite size effects etc.
- Calculation of D_2 hugoniot
  - Compare to experiments from a variety of platforms (gas guns, flyer plates, laser shocks)
  - CEIMC results are considerably more compressible



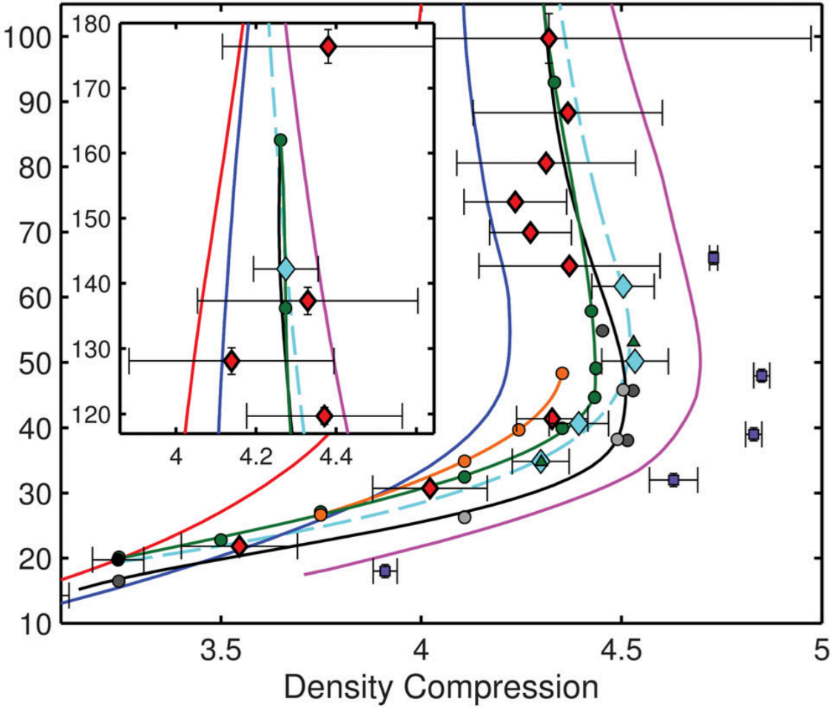
Tubman, Liberatore, Pierleoni, Holzmann and Ceperely, PRL **115**, 045301 (2015)

Why could CEIMC disagree with experiments?

- Reference State

$$2\left(E - E_{ref}\right) - \left(P + P_{ref}\right)\left(v_{ref} - v\right) = 0$$

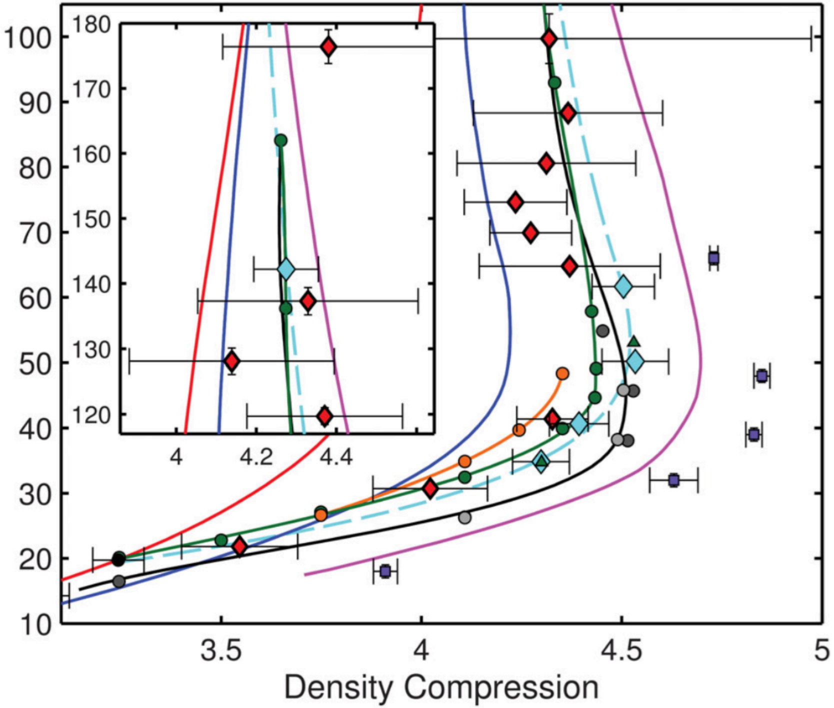
  - DMC calculation of isolated D_2 molecules is exact
  - Nuclear quantum effects are accounted for directly
  - Experimental data is used for slight correction due to initial density
  - Only question is inconsistency between this and high pressures
    - *Likely a small source of error*



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

Why could CEIMC disagree with experiments?

- Finite Size Effects
  - Electronic
    - *Similar concern to resolving the fermi surface in DFT*
    - *Not likely to bias the molecular vs atomic question*
    - *Extensively explored in Holzman, Clay, Morales, Tubman, Cepereley and Pierleoni, PRB **94**, 035126 (2016)*
  - Ionic
    - *Calculations contain only 54 ions*
    - *These finite size effects tend to over-structure a fluid*
      - Reduced degrees of freedom



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

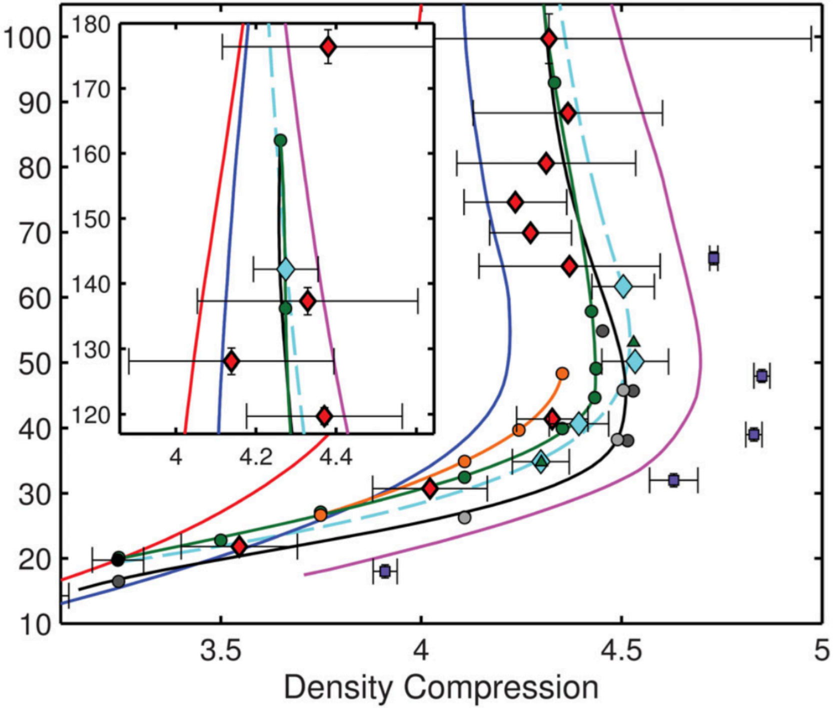
Why could CEIMC disagree with experiments?

- Electronic temperature
  - Contribution begins when gap to excited states is comparable to T
  - In general, the absence of any correction, ignoring temperature causes too few degrees of freedom
  - For dissociation of molecule, zero temperature favors molecular state

  - Tubman paper explored using thermodynamic integration type approach to add in effect using DFT

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

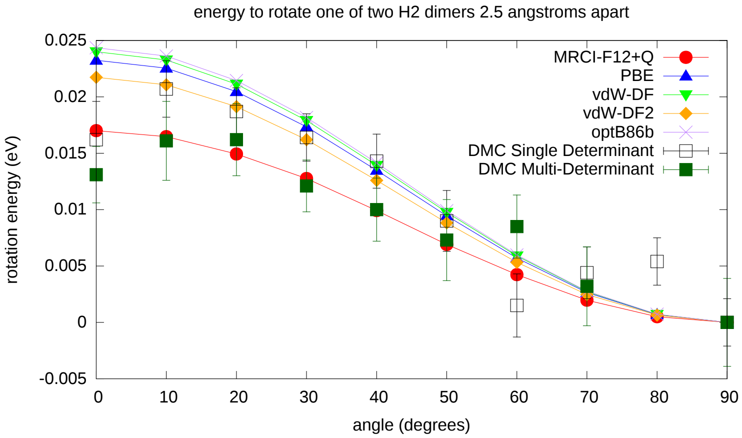
  - DFT and QMC favor different geometries, so spectra may not be comparable
    - *See Clay, McMinis, McMahon, Pierleoni, Cepereley and Morales, PRB* ***89****, 184106 (2014)*

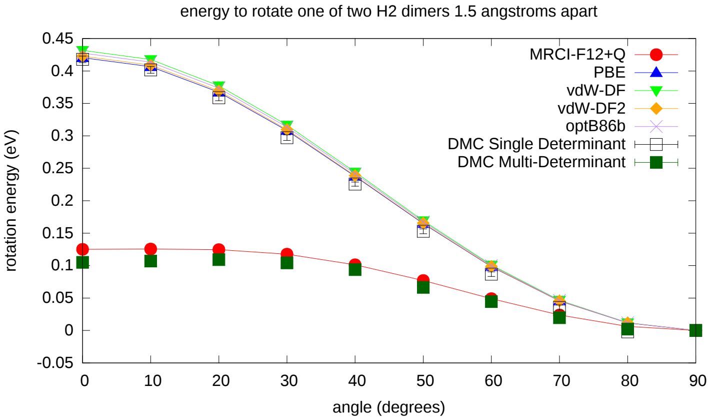


Knudson and Desjarlais, PRL **118**, 035501 (2017)

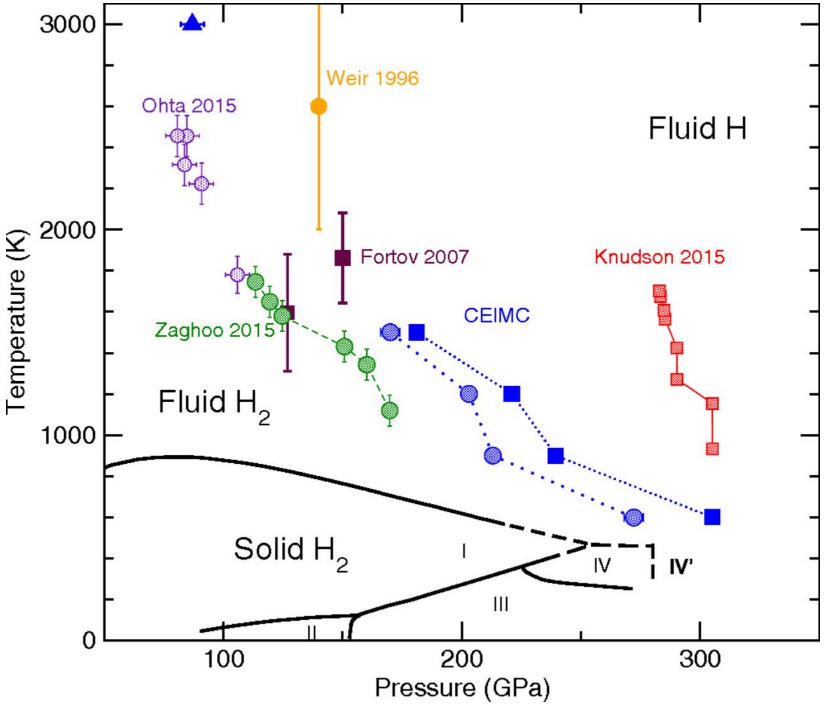
Why could CEIMC disagree with experiments?

- Nodal Surface
  - 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





Resolving differences has much potential



Pierleoni, Morales, Rillo, Holzmann, and Ceperely.
PNAS **113**, 4953 (2016)

Quantum Monte Carlo has a lot of potential for contributing to the study of WDM

- Methods are not as mature as DFT, but community is growing
- Nature of supercomputers will make calculations more routine as time goes on
- Results are interesting, but more is to be done to reach benchmark accuracy
    - Finite temperature
    - Nodal Surface
    - Larger Systems