

The Simulation of Dense Hydrogen using Coupled-Electron Monte Carlo

Fei Lin, M. Morales, DMC: University of Illinois

C. Pierleoni: L'Aquila, ITALY

K. Delaney: UCSB

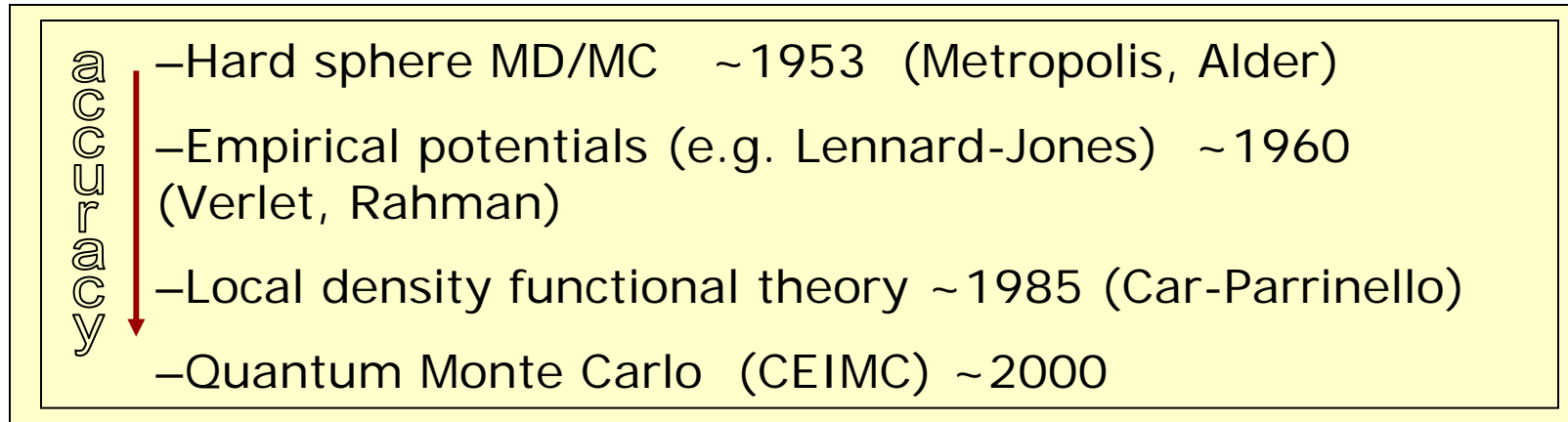
M. Holzmann: Paris

- The coupled electron-ion Monte Carlo method
- The physics of hydrogen: the atomic-molecular transition
- Conductivity of dense hydrogen

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Computer time from NCSA and ORNL (INCITE grant)

MD and MC Simulations



- Initial simulations used semi-empirical potentials.
- Much progress with “ab initio” molecular dynamics simulations where the effects of electrons are solved for each step.
- However, the potential surface as determined by density functional theory is not always accurate enough
- **QMC+MD =CEIMC/MD** is a candidate for petascale “killer app”

Quantum Monte Carlo

- Premise: we need to use simulation techniques to “solve” many-body quantum problems just as you need them classically.
- Both the wavefunction and expectation values are determined by the simulations. Correlation built in from the start.
- QMC gives most accurate method for general quantum many-body systems.
- Ceperley-Alder electronic energy is a standard for approximate LDA calculations.
- Path Integral Methods provide a exact way to include effects of ionic zero point motion
- A **variety** of stochastic QMC methods (we use them all):
 - **Variational Monte Carlo VMC (T=0)**
 - **Projector Monte Carlo (T=0)**
 - **Diffusion MC (DMC)**
 - **Reptation MC (RQMC)**
 - **Path Integral Monte Carlo (PIMC) (T>0)**
 - **Coupled Electron-Ion Monte Carlo (CEIMC)**

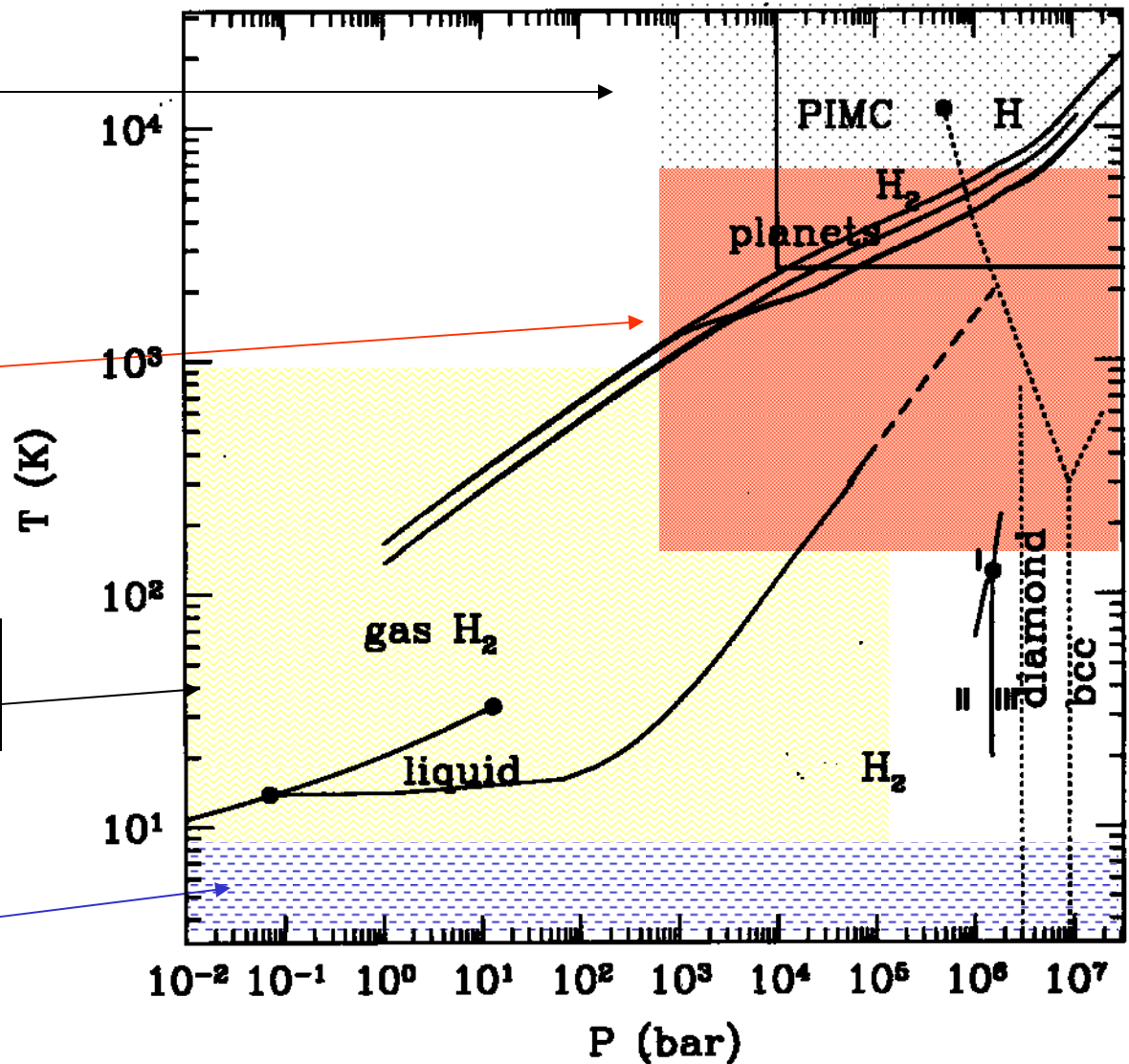
QMC methods for Hydrogen

Path Integral MC for
 $T > E_F/10$

Coupled-electron Ion
MC

Path Integral MC with
an effective potential

Diffusion MC $T=0$



Variational Monte Carlo (VMC)

(McMillan 1965)

- Put correlation directly into the wavefunction.
- Integrals are hard to do: need MC.
- Take sequence of increasingly better wavefunctions. Stochastic optimization is important!
- **Can we make arbitrarily accurate functions?** Method of residuals says how to do this.
- Recent progress with "backflow"
- No sign problem, and with classical complexity.

- Posit a wavefunction $\phi(\mathbf{R}, \mathbf{a})$
- sample $|\phi(\mathbf{R}, \mathbf{a})|^2$ with random walk.
- minimize energy or variance of $\phi(\mathbf{R}, \mathbf{a})$ with respect to \mathbf{a}

$R \equiv (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \text{"walker"}$

$$\Psi_2(R) = \text{Det}\{\phi_i(\mathbf{r}_j)\} e^{-\sum_{i<j} u_{ij}(r_{ij})}$$

$$\Psi_{n+1}(R) \approx \Psi_n(R) e^{-\underbrace{\langle \phi_n^{-1} H \phi_n \rangle}_{\text{smoothing}}}$$

smoothing

Trial functions for dense hydrogen

- Slater-Jastrow function:
$$\Psi_2(R) = \text{Det}\{\phi_k(r_j)\} e^{-\sum_{i<j} u_{ij}(r_{ij})}$$

with the orbital from a rescaled LDA calculation.

- Reoptimization of trial functions during the CEIMC run is a major difficulty in time and reliability.
- Requires a lengthy LDA calculation for each structure.
- Trial functions used:
 - backflow + three body trial function are very successful for homogeneous systems. we generalized them to many-body hydrogen: no free parameters, but only works well for the atomic phase.
 - Fast band structure solver by removing e-p cusp and putting it into the Jastrow factor. Use plane wave basis and iterative methods. PW cutoff is minimized. Works in intermediate H-H₂ phase.

Projector Monte Carlo

e.g. Diffusion Monte Carlo (DMC)

- Automatic way to get better wavefunctions.
- Project single state using the Hamiltonian

$$\phi(t) = e^{-(H-E)t} \phi(0)$$

- This is a diffusion + branching operator.
- Very scalable: each walker gets a processor.
- **But is this a probability?**
- **Yes!** for bosons since ground state can be made real and non-negative. **But** all excited states must have sign changes.
- In **exact** methods one carries along the sign as a weight and samples the modulus. This leads to the famous sign problem

$$\phi(t) = e^{-(H-E)t} \text{sign}(\phi(R,0)) |\phi(R,0)|$$

Fixed-node method

- Initial distribution is a pdf.
It comes from a VMC simulation.

$$f(R,0) = |\psi_T(R)|^2$$

- Drift term pushes walks away from the nodes.
- Impose the condition:
- This is the fixed-node BC

$$\phi(R) = 0 \quad \text{when} \quad \psi_T(R) = 0.$$

- Will give an upper bound to the exact energy, the best upper bound consistent with the FNBC.

$$E_{FN} \geq E_0$$

$$E_{FN} = E_0 \quad \text{if} \quad \phi_0(R)\psi(R) \geq 0 \quad \text{all } R$$

- $f(R,t)$ has a discontinuous gradient at the nodal location.
- Accurate method because Bose correlations are done exactly.
- Scales like the VMC method, as N^3 or better.

Reptation Monte Carlo (or VPI)

good for energy differences and properties

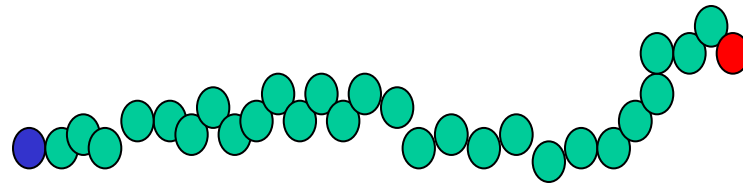
$$\Psi(\beta) = e^{-\frac{\beta}{2}H} \Psi$$

$$Z(\beta) = \langle \Psi(\beta) \Psi(\beta) \rangle = \langle \Psi e^{-\beta H} \Psi \rangle = \int dR_0 \dots dR_p \Psi(R_0) \langle R_0 e^{-\tau H} R_1 \rangle \dots \langle R_{p-1} e^{-\tau H} R_p \rangle \Psi(R_p)$$

$$E(\beta) = \frac{\langle \Psi(\beta) H \Psi(\beta) \rangle}{\langle \Psi(\beta) \Psi(\beta) \rangle} = \langle E_L(R_0) \rangle_\beta \quad \tau = \frac{\beta}{p}$$

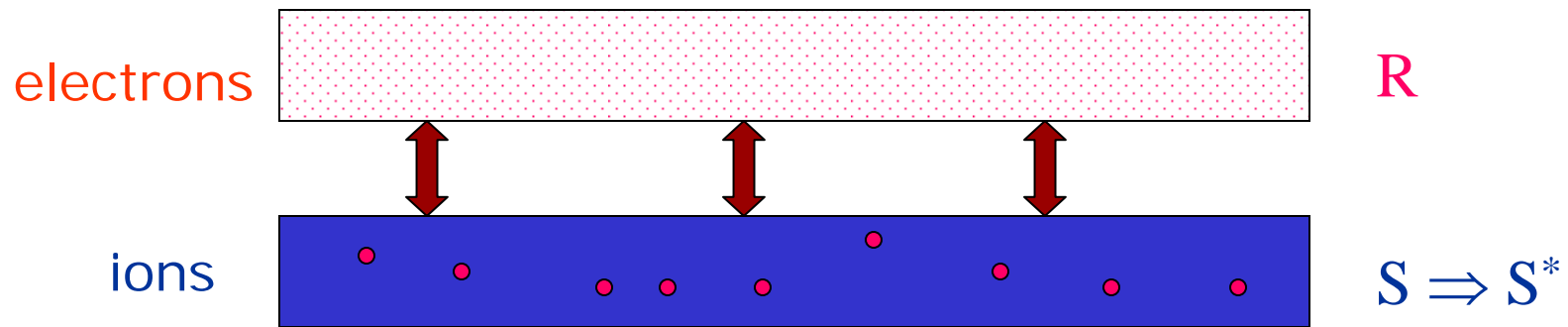
- $\psi(\beta)$ converges to the exact ground state as a function of imaginary time.
- E is an upper bound converging to the exact answer monotonically
- Do Trotter break-up into a path of p steps a la PIMC.
 - Bosonic action for the links
 - Trial function at the end points.
- For fixed-phase: add a potential to avoid the sign problem. Exact answer if potential is correct.
- Typical error is $\sim 100K/\text{atom}$
- Reptate the path: move it like a snake.

$$\boxed{(\text{Im} \nabla \ln \Psi)^2}$$



Coupled Electron-Ionic Monte Carlo: CEIMC

1. Do Path Integrals for the ions at $T > 0$.
2. Let electrons be at zero temperature, a reasonable approximation for room temperature simulations.
3. Use Metropolis MC to accept/reject moves based on QMC computation of electronic energy



The "noise" coming from electronic energy can be treated without approximation: the penalty method.

The Penalty method

DMC & Dewing, J. Chem. Phys. 110, 9812(1998).

- **Assume** estimated energy difference Δe is **normally distributed*** with variance σ^2 **and the correct mean.**

$$\langle \Delta e \rangle = \Delta E$$

$$\langle [\Delta e - \Delta E]^2 \rangle = \sigma^2$$

*central limit theorem for $\sigma < \infty$

- $a(\Delta e; \sigma)$ is acceptance ratio.
- average acceptance $A(\Delta E) = \langle a(\Delta e) \rangle$
- We can achieve detailed balance: $A(\Delta E) = \exp(-\Delta E) A(-\Delta E)$
if we accept using: $a(x, \sigma) = \min [1, \exp(-x - \sigma^2/2)]$
- $\sigma^2/2$ is "penalty" . Causes extra rejections.
- Large noise (order $k_B T$) is more efficient than low noise, because the QMC will then be faster.

A feature of Monte Carlo?

averages are almost free.

Suppose we have an extra parameter “q” to sum over.

$$E(s) = \frac{1}{M} \sum_{i=1}^M E(s; q_i)$$

- In a deterministic calculation, this will multiply CPU time by M.
- This extra parameter will not slow down the calculation by Monte Carlo: it is just one more variable to average over.
- We start up M calculations on M separate processors for different values of q: they all serve to reduce the error bar.
- Inefficiency comes from “start up” costs: e. g. Metropolis warm-up or initializations.

Types of averaging:

1. Path Integrals for ions (particularly for protons or light ions)

(M_1 time slices to average over.)

2. k-point sampling (integrate over Brillouin zone of supercell). Twist averaged boundary conditions converge much faster than periodic boundary conditions for metals.

(M_2 k-points)

- In explicit methods such as CP-MD these extra variables will increase the CPU time by M_1M_2 .
- With QMC there will be little increase in time if imaginary time and/or k are simply new variables to average over.

The result is a code scaling well to thousands of nodes and competitive with Car-Parrinello MD.

Twist averaged boundary conditions

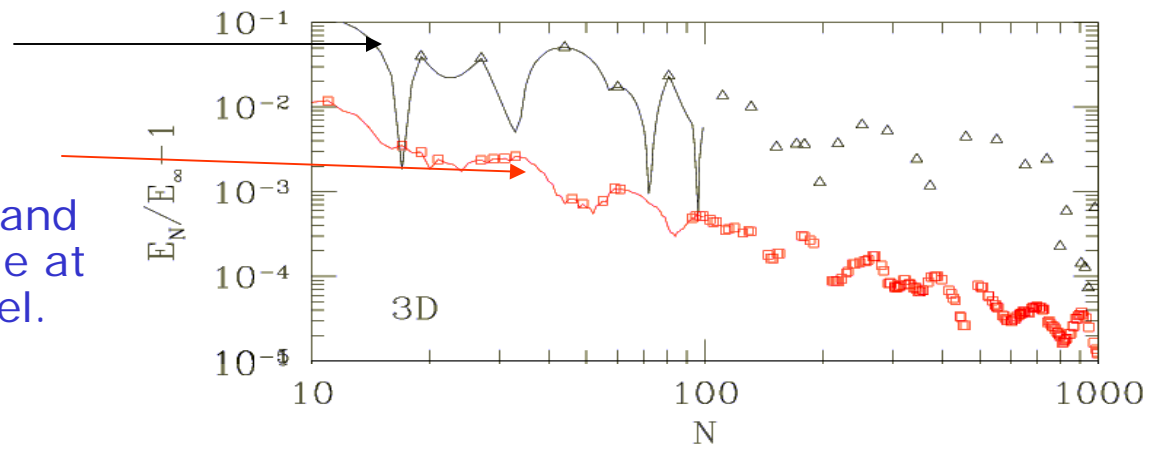
- In periodic boundary conditions, the wavefunction is periodic \Rightarrow Large finite size effects for metals because of fermi surface.
- In twist averaged BC, we use an arbitrary phase θ as $r \rightarrow r+L$
- Integrate over all phases, i.e. Brillouin zone integration.
- Momentum distribution changes from a lattice of k-vectors to a fermi sea.
- Eliminates single-particle finite-size effects.

$$\Psi(x + L) = e^{i\theta} \Psi(x)$$

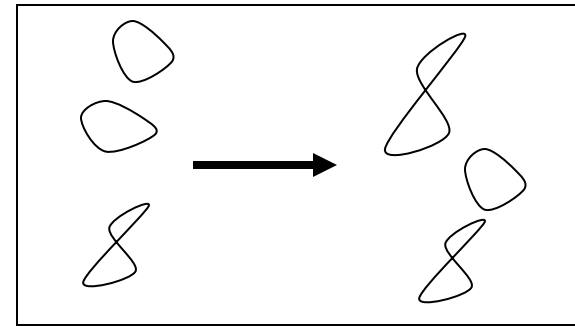
$$\bar{A} = \frac{1}{(2\pi)^3} \int_{-\pi}^{\pi} d^3\theta \langle \Psi_{\theta} A \Psi_{\theta} \rangle$$

Error with PBC
Error with TABC

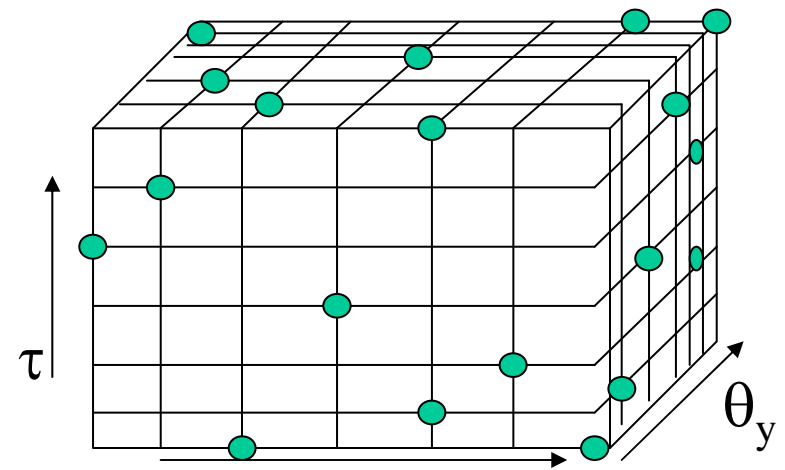
Error is zero in the grand canonical ensemble at the mean field level.



- Make a move of the protonic paths
- Partition the 4D lattice of boundary conditions ($\theta_x \theta_y \theta_z$) and imaginary time (τ) in such a way that each variable is uniformly sampled (stratified)
- Send them all out to M separate processes
- Do DMC to get energy differences and variances
- Combine to get global difference and variance.



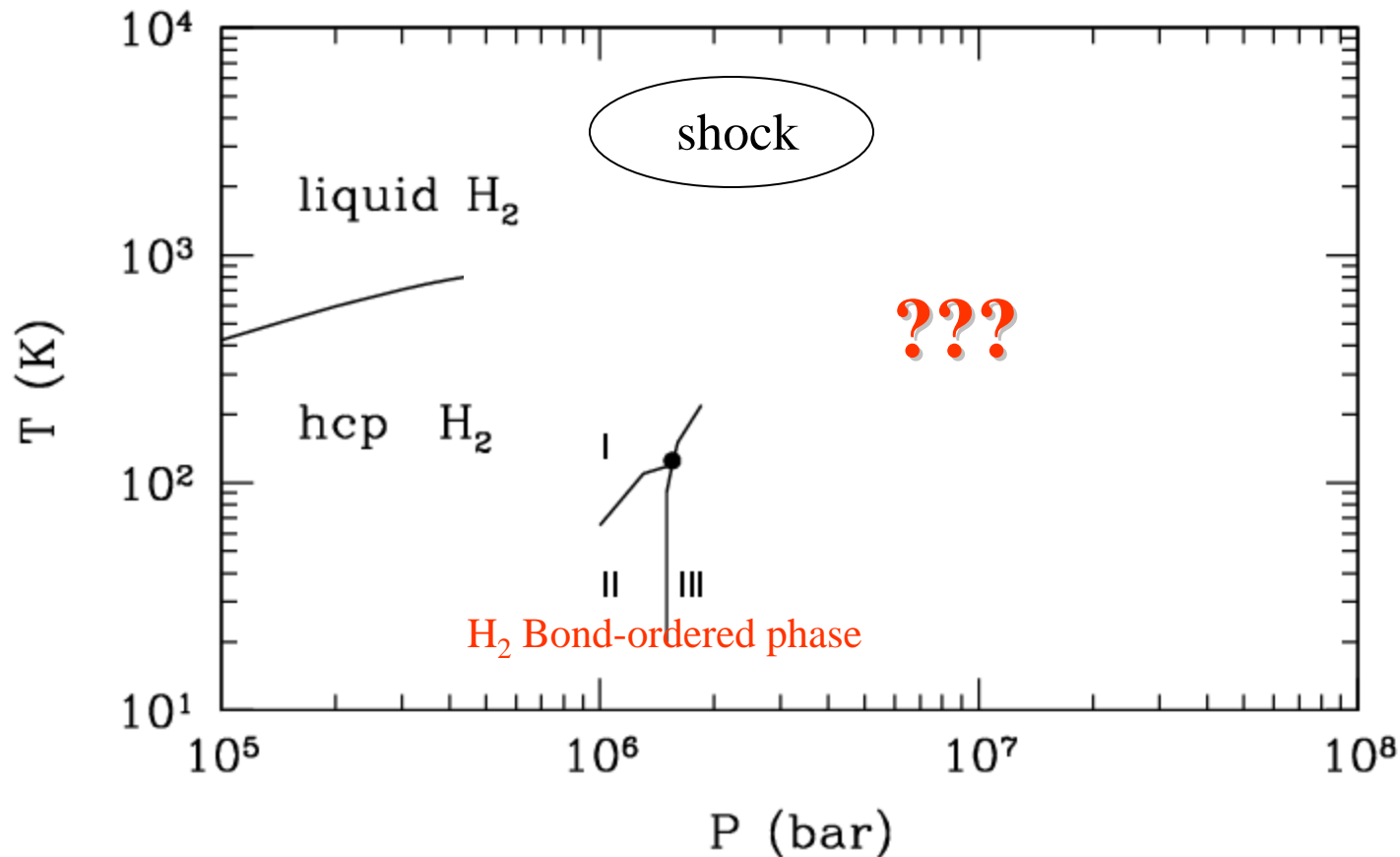
$$R_\tau \rightarrow R'_\tau$$



$$\Delta E_{BO} = \frac{1}{M} \sum E_{\theta, \tau}$$

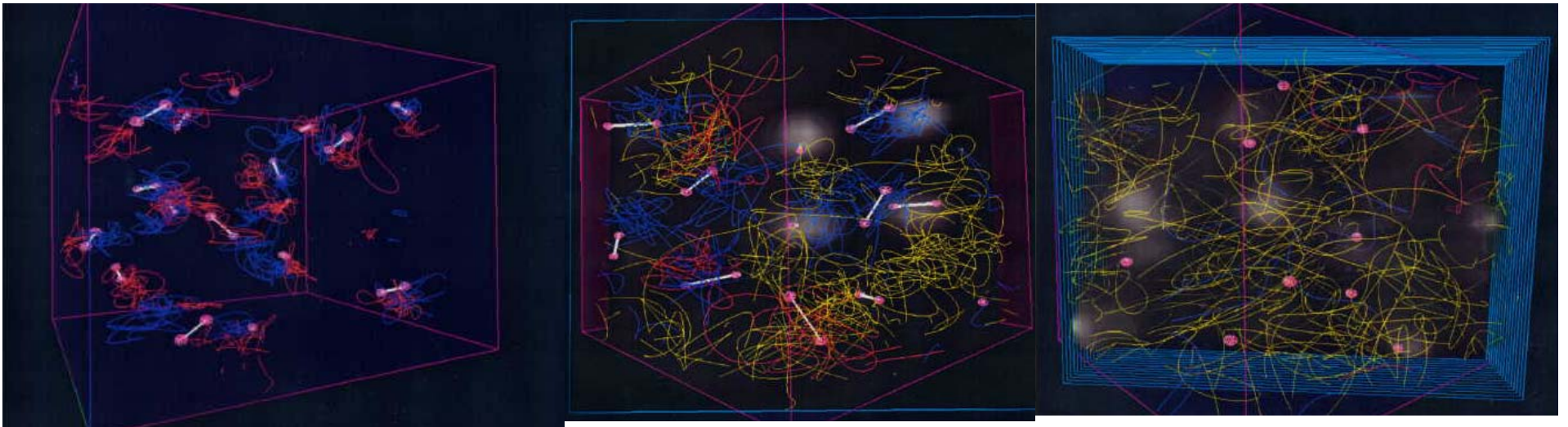
$$\sigma^2 = \frac{1}{M^2} \sum \sigma_{\theta, \tau}^2$$

Experimentally-known High Pressure Phase Diagram of H



- Wigner-Huntington (1935) predicted that at high enough pressure hydrogen will become a metal.
- Experiments have not reached (definitively) that pressure.

Evolution of hydrogen in PIMC



$r_s=4.0$

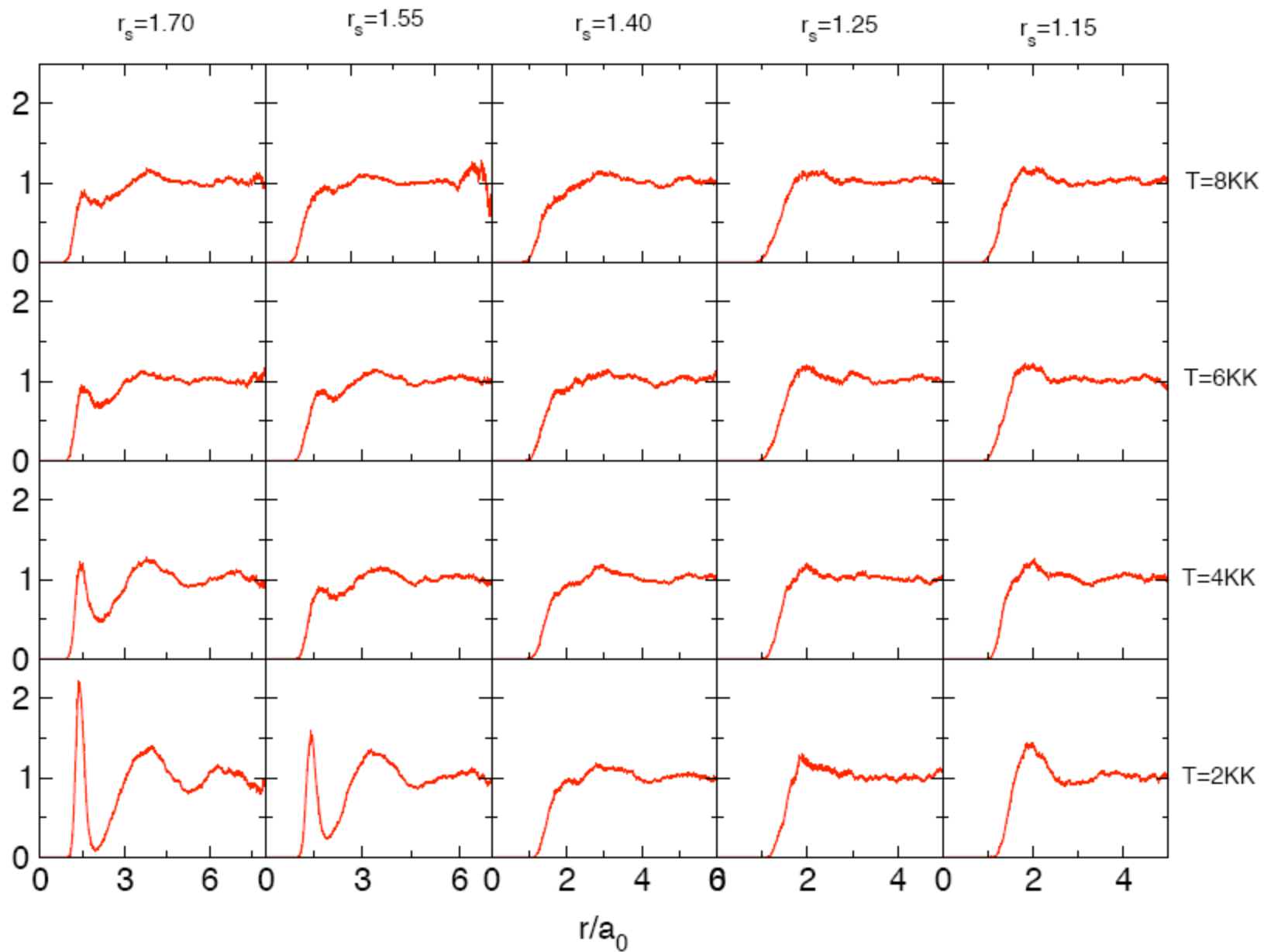
$r_s=1.86$

$r_s=1.60$

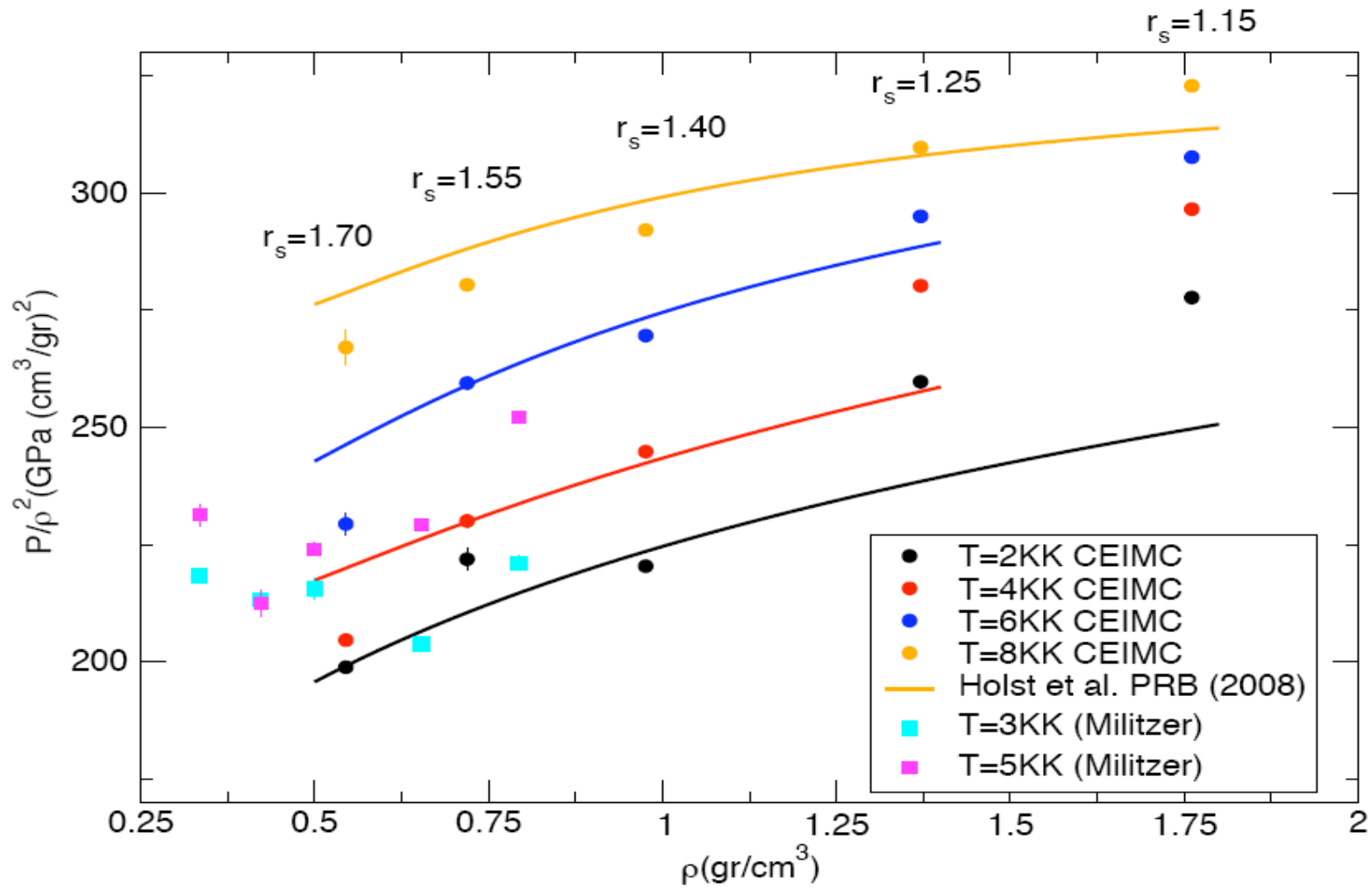
$T=5000\text{K}$

liquid hydrogen

proton-proton pair correlation function



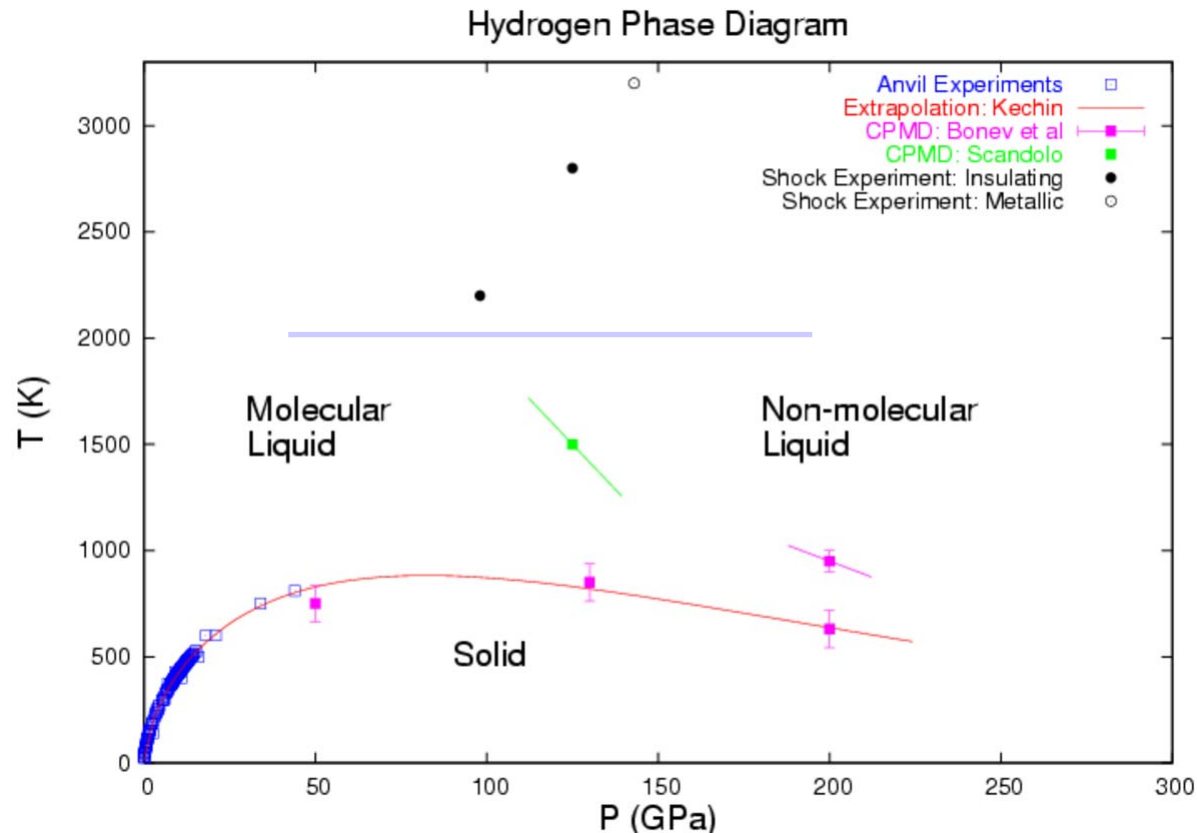
EOS: CEIMC vs BOMD



Planetary calculations will require P to 1% !

Plasma Phase Transition

- Study nature of transition from molecular to non-molecular fluid using CEIMC: phase transition or cross-over?
- Simulations at $T=2000K$ with $P=50-200GPa$



CEIMC Simulations

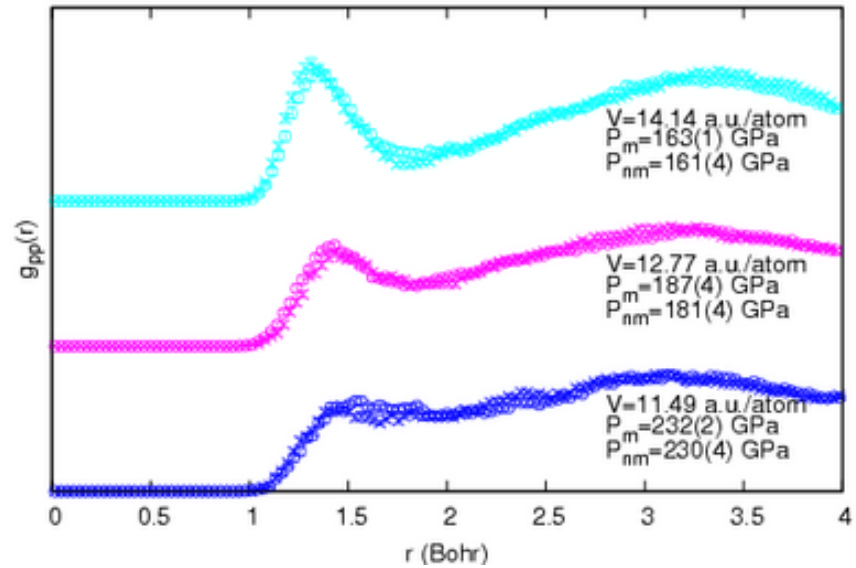
- VMC: Hysteresis; probably 1st order transition.
- RQMC: No hysteresis; continuous transition.
- VMC trial function has difficulty with the mixed H₂-H state.

$$N_p = N_e = 54$$

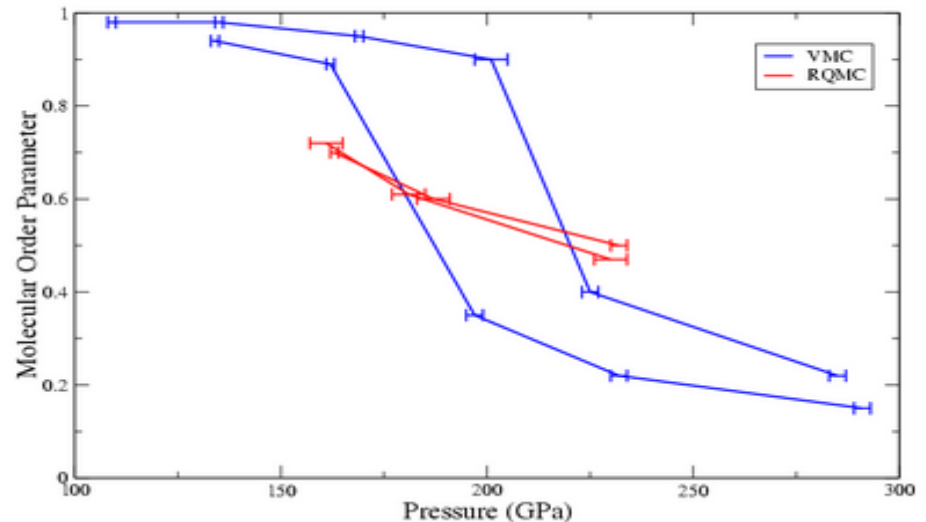
H₂ order parameter

$$g(r) = \lambda g_{mol}(r) + (1 - \lambda) g_{nonmol}(r)$$

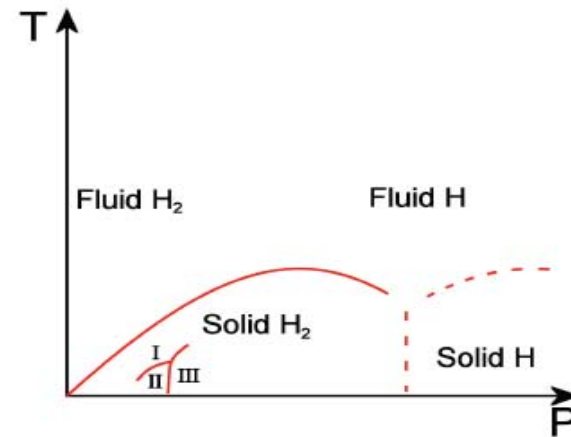
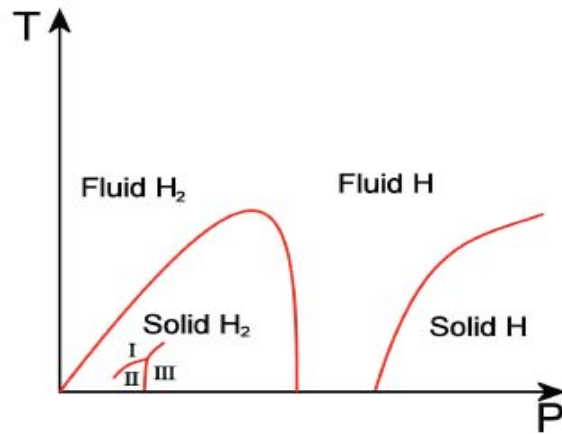
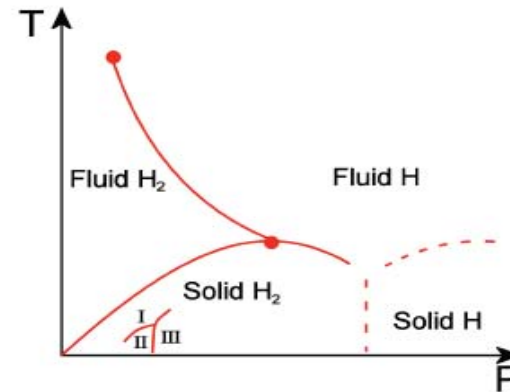
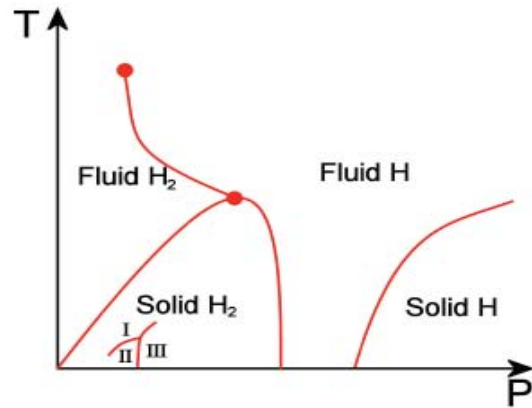
Collection of $g_{pp}(r)$ s for T=2000K using RQMC



Molecular to Non-molecular Fluid Phase Transition



Possible Phase Diagrams for high pressure hydrogen



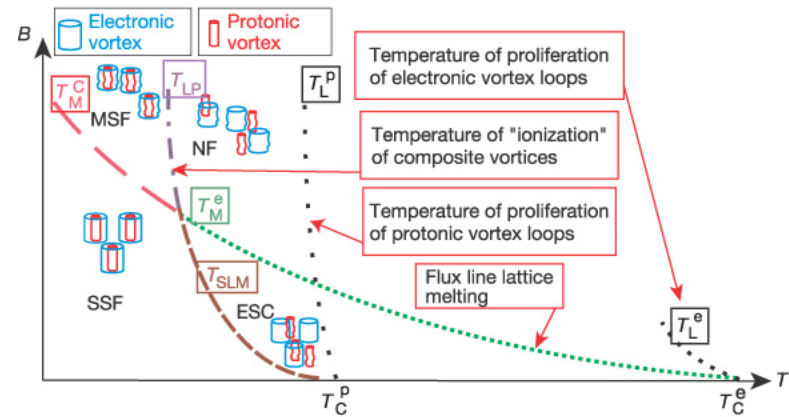
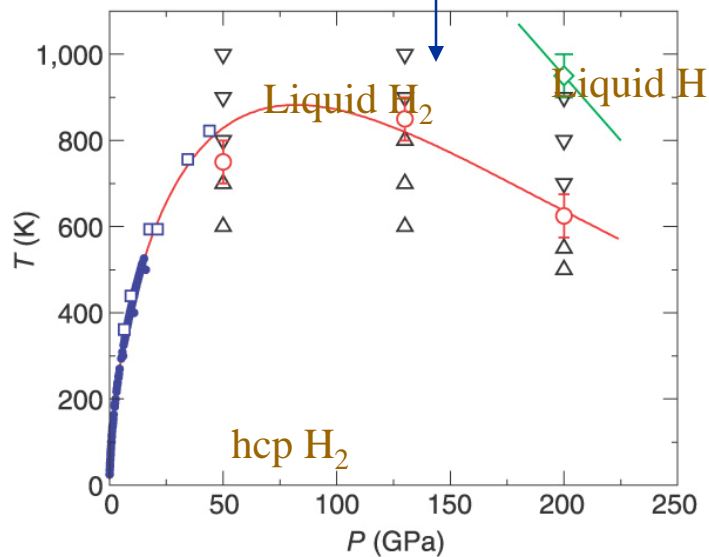


07 October 2004

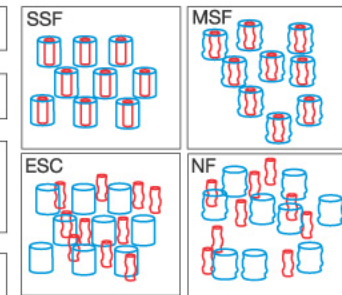
A quantum fluid of metallic hydrogen suggested by first-principles calculations S. A. BONEV, E. SCHWEGLER, T. OGITSU & G. GALLI

liquid

A superconductor to superfluid phase transition in metallic hydrogen E. BABAEV, A. SUDBØ & N. W. ASHCROFT



- MSF: Matter state: *Metallic superfluid*
Vortex matter: *"Liquid"*
- NF: Matter state: *Normal fluid*
Vortex matter: *"Line plasma"*
- SSF: Matter state: *Superconducting superfluid*
Vortex matter: *"Molecular crystal"*
- ESC: Matter state: *Electronic superconductor*
Vortex matter: *"Sublattice liquid"*



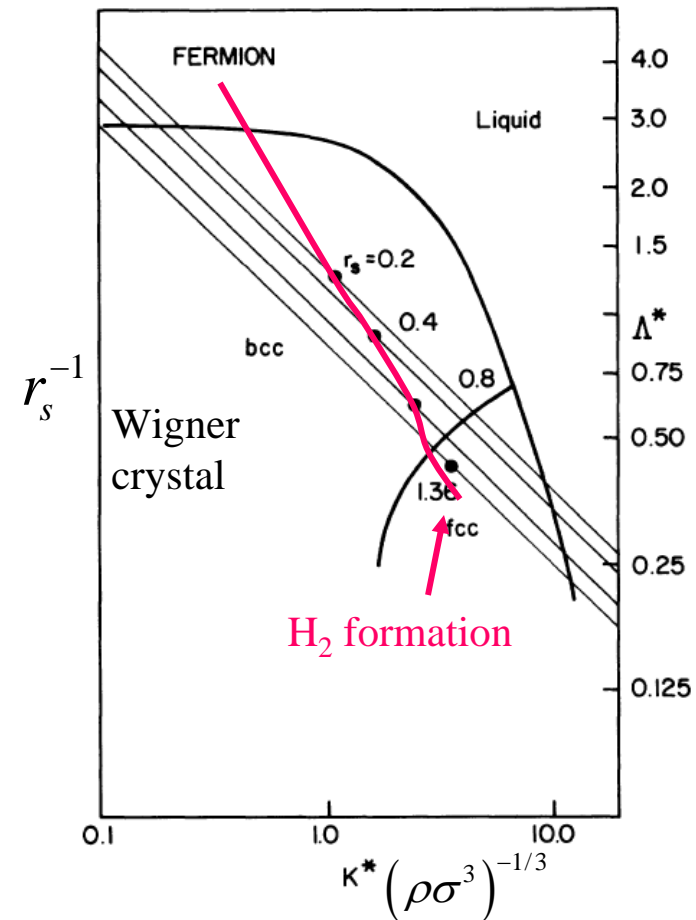
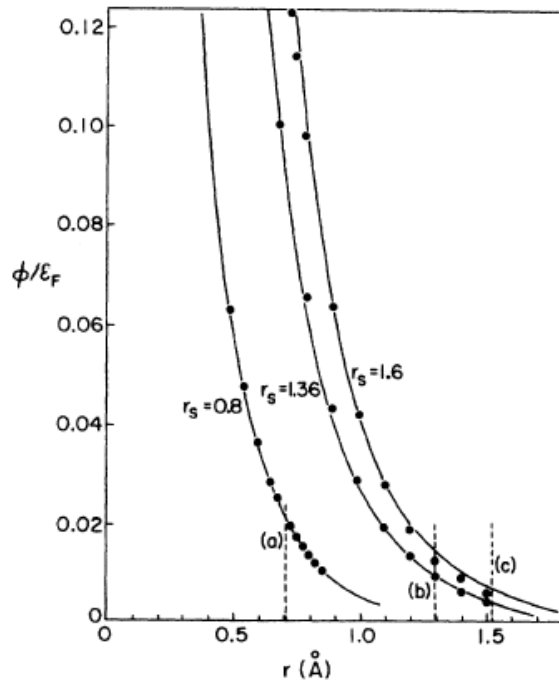
Could hydrogen be a quantum fluid like helium?

Why liquid?

Screened Coulomb potential

Electrons screen p-p
interaction

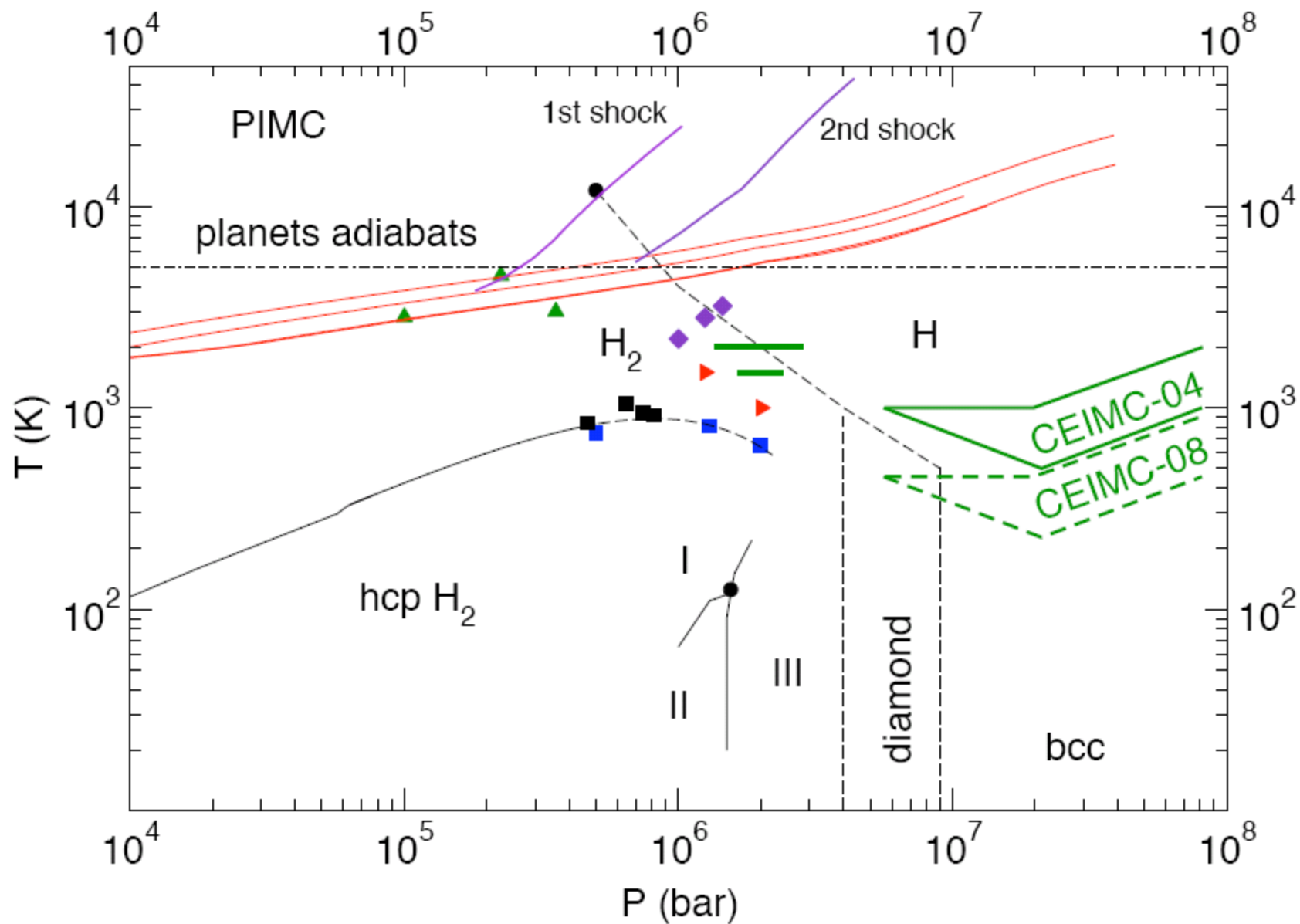
$$H_{pp} = -\sum_i \frac{\hbar^2}{2m} \nabla^2 + \sum_{i<j} v(r_{ij}) \quad v(r) = \frac{\epsilon\sigma e^{-r/\sigma}}{r} \quad \sigma \propto r_s^{-1/2}$$



K.K. Mon et al, Phys. Rev. B 21,2641 (1980)

DMC et al. Phys. Rev. B 16, 3081 (1976)

Hydrogen phase diagram



Computation of the Conductivity

- World line method can use “inverse Laplace transform” but there are problems implementing in our method
- We use linear response formula for conductivity:

$$\sigma(\omega) = \frac{2\pi(1 - e^{-\beta\omega})}{\omega} \sum_m \left| \langle m | \hat{J} | 0 \rangle \right|^2 e^{-\beta\delta E_m} \delta(\delta E_m - \omega)$$

\hat{J} = current operator, δE_m = excitation energy

- We determine an excited states basis set with a DFT calculation considering particle-hole excitations.
- Using reptation, we find the needed excitation energies and current matrix elements (including correlation)

VMC Calculation of excited-state energies

Correlation Function MC: J. Chem. Phys. **89**, 6316 (1988).

- Construct a basis of trial functions spanning excited states in question. $\{f_i(R)\} \quad 1 \leq i \leq M$
- Using VMC calculate all the matrix elements. Must use a bosonic sampling function.

$$P(R) = \sum_n |f_n|^2$$

- Find lowest energy in this basis
- Solve the generalized eigenvalue problem:

$$H_{ij} C_j^\lambda = E^\lambda N_{ij} C_j^\lambda$$

$$N_{ij} \equiv \langle f_i | f_j \rangle = \left\langle \frac{f_i^*(R) f_j(R)}{P(R)} \right\rangle$$

$$H_{ij} \equiv \langle f_i | H | f_j \rangle = \left\langle \frac{f_i^*(R) f_j(R) E_{ij}(R)}{P(R)} \right\rangle$$

- Then E_k is the best upper bound spanned by the basis functions.
- Zero variance applies also to excited states.

Projector Monte Carlo method

- The time-evolved basis approaches the exact eigenfunctions:

$$f_i(R, t) = e^{-tH/2} f_i(R)$$

- Using bosonic DMC (no nodes) calculate the N and H as a function of imaginary time. Note, $H = -dN/dt$.

$$N_{ij}(t) \equiv \left\langle f_i \left| e^{-t\hat{H}} \right| f_j \right\rangle = \left\langle f_i^* (R(t + t_0)) f_j (R(t_0)) \right\rangle$$

- Use same guiding function for importance sampling.
- Solve the generalized eigenvalue problem:

$$H_{ij}(t) a_j^\lambda = E(t)^\lambda N_{ij}(t) a_j^\lambda$$

- Then $E^\lambda(t)$ approaches the exact λ^{th} energy exponentially fast and from above (MacDonald's Theorem)
- Can use with reptation Monte Carlo: N and H are computed at the ends of the reptile.

Computation of the Conductivity

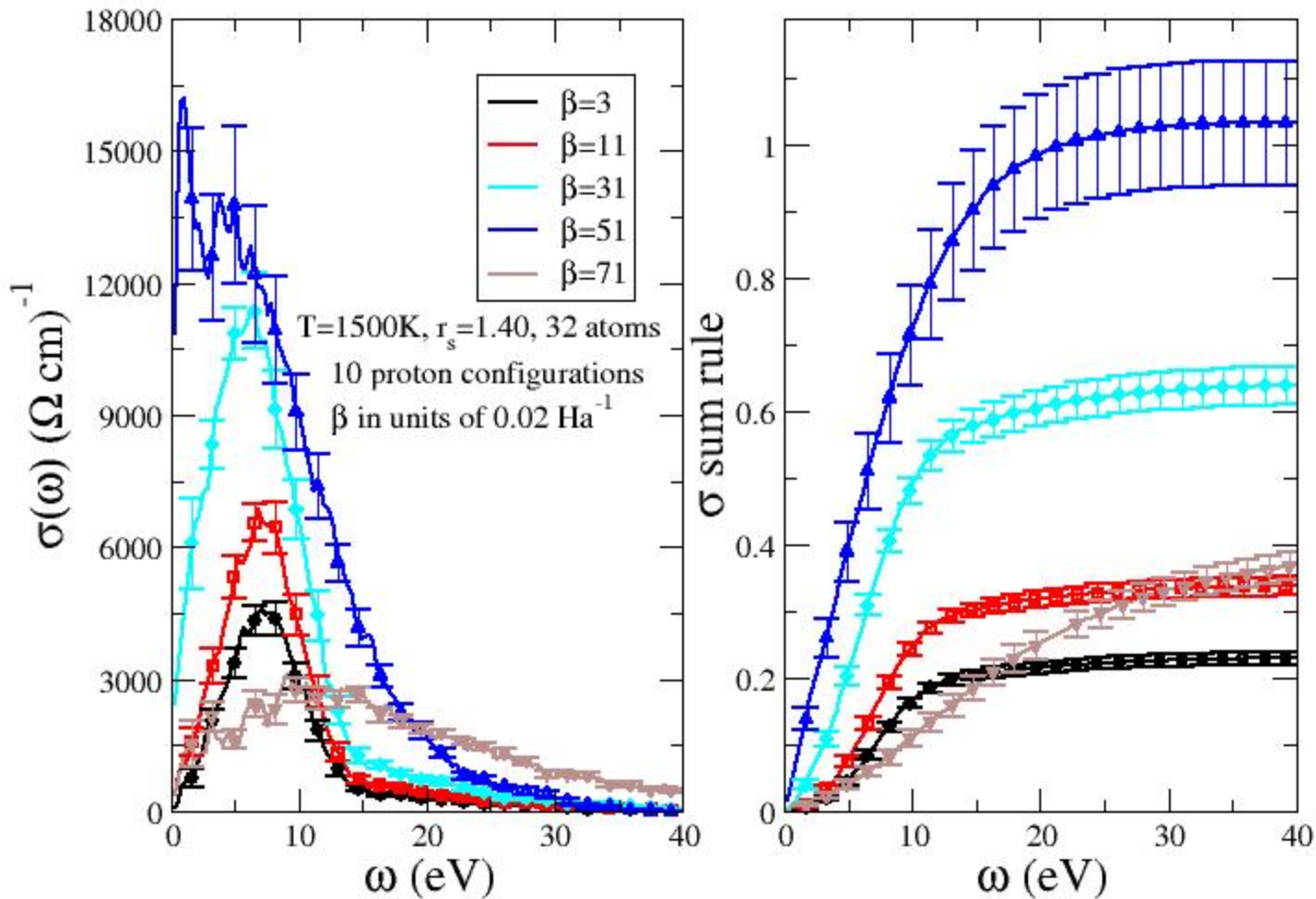
- linear response formula for conductivity:

$$\sigma(\omega) = \frac{2\pi(1 - e^{-\beta\omega})}{\omega} \sum_m \left| \langle m | \hat{J} | 0 \rangle \right|^2 e^{-\beta\delta E_m} \delta(\delta E_m - \omega)$$

\hat{J} = current operator, δE_m = excitation energy

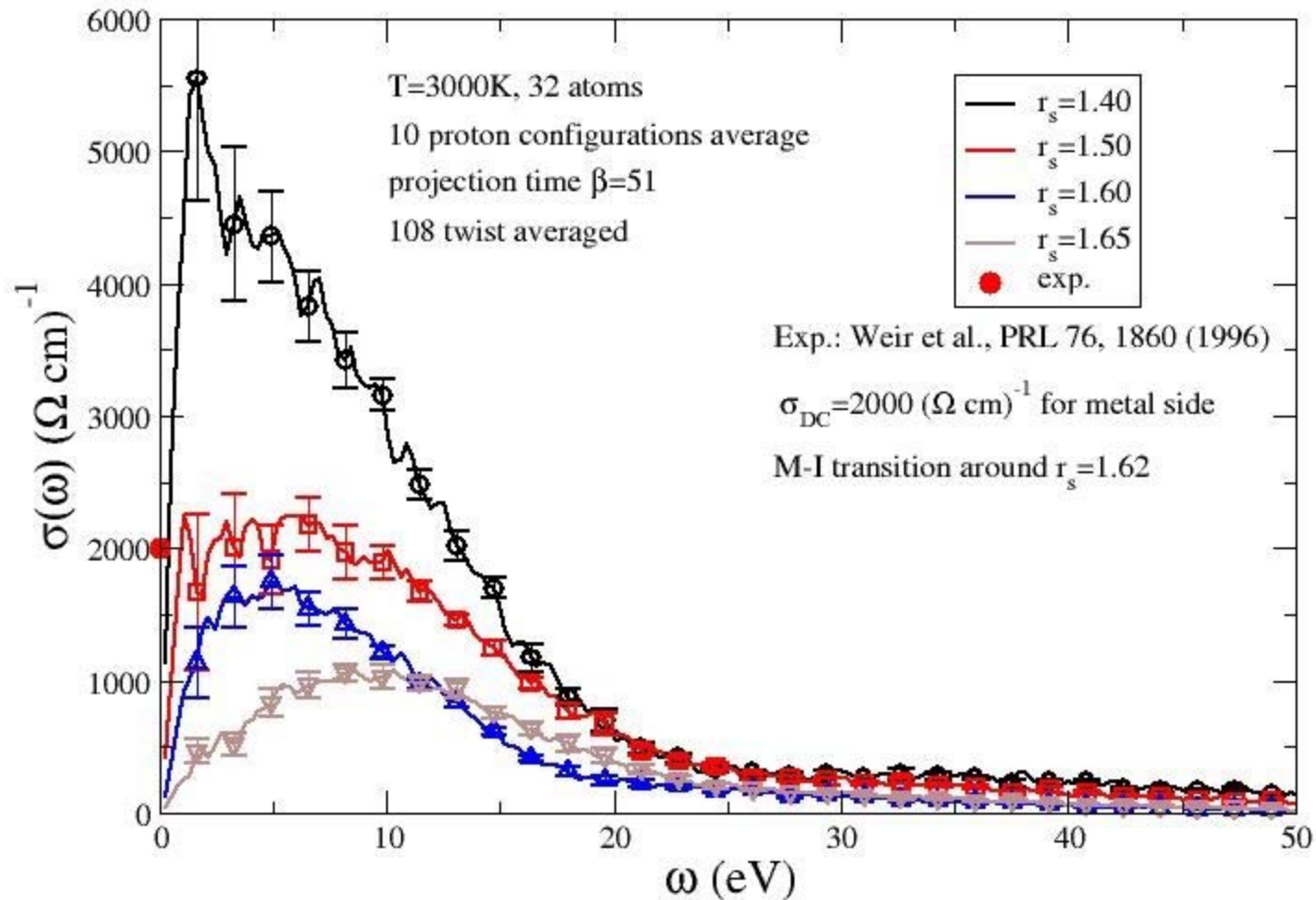
- We determine an excited states basis set with a DFT calculation considering particle-hole excitations. Make all HOMO-LUMO excitations with $\delta E < E_{\text{cut}}$
- Using CFQMC, we find the needed excitation energies and current matrix elements (including correlation)
- Average over proton positions and "twists."

Conductivity and sum rules vs. different projection times, β



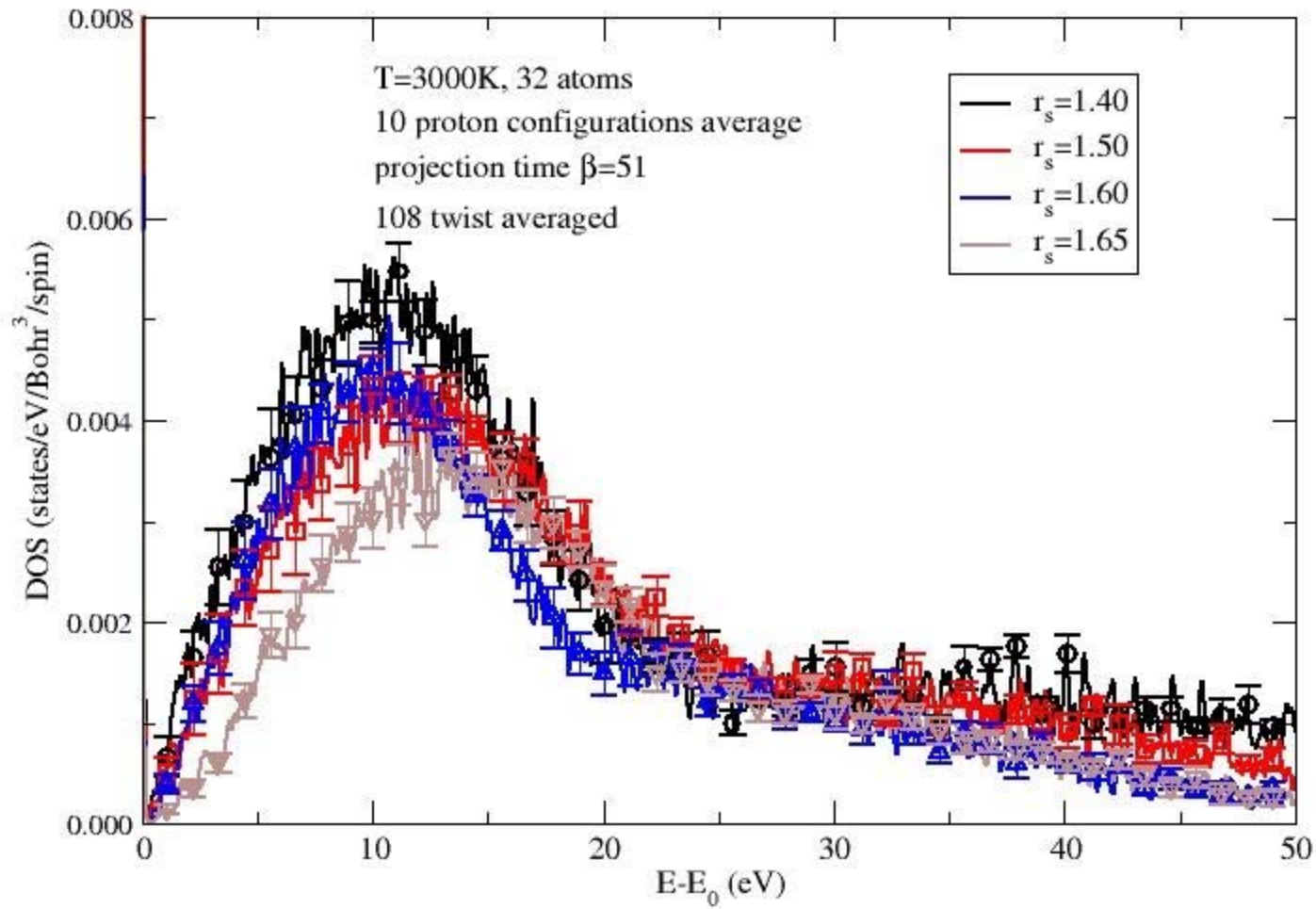
$$\frac{2m}{\pi e \rho} \int_0^{\infty} d\omega \sigma(\omega) = 1$$

Metal-insulator transition with density variation



$13,000 (\Omega \text{ cm})^{-1}$ DFT Pfaffenseller et al, *J Phys. Cond. Matt* 9, 11023 (1997)

DOS for different densities at 3000K



- QMC today is competitive with other methods for dense hydrogen and potentially much more accurate.
- Conductivity seems feasible using Green-Kubo formula.
- Progress in these simulations in last 40 years, has come from both:
 - Computer power: this method scales well with number of processors
 - Algorithmic power: better trial functions, QMC methods
- We are now in position to do much more accurate simulation of hydrogen, helium, mixtures...
- More work needed in algorithms to get higher accuracy, treat larger systems, and heavier elements allowing:
 - Benchmarks that validate cheaper approaches
 - OR
 - Replace more approximate approaches.