Coupled Electron-Ion Monte Carlo Study of Hydrogen Phases

Kris Delaney, David Ceperley
University of Illinois at Urbana-Champaign

Carlo Pierleoni
Universita del l’Aquila, l’Aquila, Italy

Supported by NSF DMR 04-04853 and NSF DMR 03-25939 ITR
Overview

• Introduction to Coupled Electron-Ion Monte Carlo (CEIMC)

• Trial wavefunction

• Open problems in hydrogen EoS

• Application of CEIMC to H

• Liquid-liquid phase transition results
Introduction to CEIMC

- Generate Boltzmann weights of nuclear configurations using MC sampling
- Supports a range of temperatures, \( T < 10,000 \text{K} \)
- QMC methods usually limited to \( T = 0 \text{K} \) only
- PIMC for high \( T \) (\( \sim 3,000 \text{K} \)) only

Couple MC simulation of electrons and nuclei:

- Electrons at \( T = 0 \text{K} \)
- Nuclei classical or quantum (PI) at finite \( T \)

Supports a range of temperatures, \( T > 100,000 \text{K} \)

Using MC sampling

Generate Boltzmann weights of nuclear configurations
CEIMC Details

• Classical Nuclei:
  – Metropolis acceptance ratio for nuclear moves:
    \[ A = \min\{1, \exp(-\beta \Delta E(s,s'))\} \]
  – Depends on \( \Delta E(s,s') = V(s) - V(s') \), B.O. energies

• B.O. energies:
  – VMC or RQMC
  – RQMC: Projector method with no mixed estimator
    Energy difference unbiased

• Twist-averaged boundary conditions (TABC) to reduce finite-size effects. Analogous to \( k \)-integration.
Penalty Method

• B.O. energy difference is noisy

• Metropolis acceptance ratio is biased

• Adjust using “Penalty Method”:
  – Satisfy detailed balance on average
  – Acceptance ratio becomes

\[
A = \min \left[ 1, \exp \left( -\beta \left( \Delta E(s, s') + \frac{\sigma^2}{2} \right) \right) \right]
\]

  – Tolerates noisy estimates of energy differences
  – In practice, \( \sigma \) estimated \( \Rightarrow \) further terms

• Correlated sampling methods \( \Rightarrow \) noise lowered
  \( \Rightarrow \) fewer noise rejections
Why use CEIMC?

- **MD**: Samples dynamics but larger cells and longer simulations required
- **MC**: Fast exploration of configuration space, not constrained by real dynamics. No time step error.

- **LDA** H fluid pair correlation functions less structured than CEIMC; match CEIMC for $2T$.
  - PRL 93, 146402 (2004)
- **LDA/GGAs** predict wrong metallization pressure of H at $T=0K$
B.O. Wavefunction

- Fast + transferable wavefunction required, permit many nuclear moves
- Solve single-particle Hamiltonian with model effective potential
- Eigenvectors used in Slater-Jastrow wavefunction

- Potential type?

\[ V(r) = \frac{e^{-\alpha r}}{r} \]

---

8-atom SC cell

16-atom mHCP cell
Application to Hydrogen

- Current phase diagram:

  ![](Hydrogen Phase Diagram)

- Open problems:
  - Liquid-liquid phase transition
  - Shape of melt curve
Results

- Simulation details:
  - 32 atoms, NVT ensemble
  - $T = 2000K$
  - $P = 50 – 200 \text{ GPa}$
  - VMC for $\Delta E$
  - 1000 twist angles

- All state points begin with molecular fluid
Conclusions

• Molecular dissociation occurs at T=2000K in CEIMC. Appears to be continuous.

• New wavefunction used in CEIMC, appears fast and accurate

• Future work:
  – Begin with other initial configurations
  – Assess size of hysteresis effects
  – Further assess size of finite-size effects
  – Investigate metallization of fluid
  – Other temperatures
  – Quantum nuclei