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Coupled Electron Ion Monte Carlo Calculations of Atomic Hydrogen

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Abstract

We present a new Monte Carlo method which couples Path Integral for finite temperature protons with Quantum Monte Carlo for ground state electrons, and we apply it to metallic hydrogen for pressures beyond molecular dissociation. This method fills the gap between high temperature electron-proton Path Integral and ground state Diffusion Monte Carlo methods. Our data exhibit more structure and higher melting temperatures of the proton crystal than Car-Parrinello Molecular Dynamics results using LDA. We further discuss the quantum motion of the protons and the zero temperature limit.

Key words: Quantum Monte Carlo, metallic hydrogen

PACS: 05.30.Lq, 71.10.+x, 64.30.+t, 02.70.Lq

1. Introduction

Quantum Monte Carlo (QMC) methods have been developed for accurately solving the many-body Schrödinger equation. Zero temperature Variational Monte Carlo (VMC) and Diffusion Monte Carlo (DMC), and finite temperature Path Integral Monte Carlo (PIMC) are currently the most accurate and general methods for computing static properties of a quantum system [1,2]. They have been successfully applied to simple quantum many-body systems, such as the electron gas, hydrogen, and helium.

Recently, there have been new attempts[3,4,5] to calculate properties of disordered systems such

as liquid hydrogen within QMC. For this system, VMC/DMC and PIMC are computationally too inefficient to provide definite answers, e.g. regarding the nature of the melting transition from liquid to solid or metal to insulator. Whereas PIMC calculations have been done at comparatively high temperatures [6], this method becomes computationally inefficient at temperatures lower than roughly 1/20 of the Fermi temperature. Zero temperature calculations (VMC, DMC) have been used for ground state calculations where both electronic and protonic degrees of freedom are treated quantum mechanically [7,8]. However, the convergence of these calculations suffers from the different masses of protons and electrons which introduce two time scales differing by three orders of magnitude, and, more important, low temperature properties are inaccessible by these ground

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state methods. To fill this gap, the Coupled Electron-Ion Monte Carlo (CEIMC) has been developed [3,4] to combine a classical or quantum Monte Carlo simulation of the nuclei at non-zero temperature with a QMC calculation for the electronic energies where the Born-Oppenheimer approximation helps to overcome the time scale problem.

In Ref. [5], the CEIMC method has been applied to determine the equation of state of hydrogen for temperatures across the melting of the proton crystal. More structure and higher melting temperatures of the proton crystal compared to Car-Parrinello Molecular Dynamics (CPMD) results using LDA[9] have been found. In this paper, we shortly summarize the method and the results as reported in Ref. [5] and discuss in more detail the quantum effects of the protons [10,11].

2. Method

In the CEIMC method, the proton degrees of freedom are advanced by a Metropolis algorithm in which the energy difference between the actual state S and the trial state S' is computed by a Quantum Monte Carlo calculation. The energies of the states are calculated within the Born-Oppenheimer approximation, where the electrons are assumed to remain in the ground state with respect to the actual protonic positions. Since the Born-Oppenheimer energies $E(S)$ and $E(S')$ have to be sampled by a QMC calculation, they are affected by statistical noise which would bias the Monte Carlo sampling of the protons. At first sight one might expect that for an unbiased calculation one will need to reduce the accuracy of the energy difference $E(S) - E(S')$ much below $k_B T$. However, it has been shown that unbiased sampling of the proton configurations can be efficiently achieved by using the penalty method[13], a generalization of the Metropolis algorithm, where detailed balance is satisfied on average.

Since only differences of electronic energies are needed, we sample the electronic degrees of freedom according to the sum of the electronic distribution functions (*e. g.* the square of the trial wave function in VMC) for the S and S' states, and we compute the energies for the two states as correlated sampling averages[3,4]. For the typical size of the proton

moves (between 0.01 Å and 0.5 Å for classical protons) this method is much more efficient than performing two independent electronic calculations [3,4].

An essential part of the CEIMC method is the choice of the trial wavefunction needed to calculate the Born-Oppenheimer energies. Variational Monte Carlo depends crucially on the quality of the trial wavefunction. To go beyond VMC, we implemented a Reptation Quantum Monte Carlo algorithm (RQMC)[12] to sample more accurately the electronic ground state. Similar to DMC, RQMC projects the trial wavefunction on to the ground state within the Fixed-Node approximation. A high quality trial wave function is important to relax to the ground state with a very limited number of time slices and to provide accurate nodes. RQMC, being a Metropolis based method, is more easily used to compute energy differences; conversely, the correlated sampling method within DMC is more involved because of the branching step.

To reduce finite size effects in metallic systems, we average over twisted boundary conditions (TABC) when computing electronic energies within CEIMC (*i.e.* we integrate over the Brillouin zone of the super cell)[15,4].

Quantum effects for protons are relevant at high pressure. We represent protons by imaginary time path integrals without considering the statistics of the protons. (those effects are negligible in this temperature-density range.) For efficiency, it is important to minimize the number of protonic time slices. We have used the pair action of an effective proton-proton potential and treated the difference between the true Born-Oppenheimer energy and the effective potential with the primitive approximation[2]. When coupled with TABC, rather than using all the k -points for each protonic time slice, we can, randomly assign a subset of k -points to each protonic slice without introducing a detectable systematic effect.

3. Results

Comparison of CEIMC with CPMD We first consider classical protons. For classical protons it is possible to compare the CEIMC results with previous

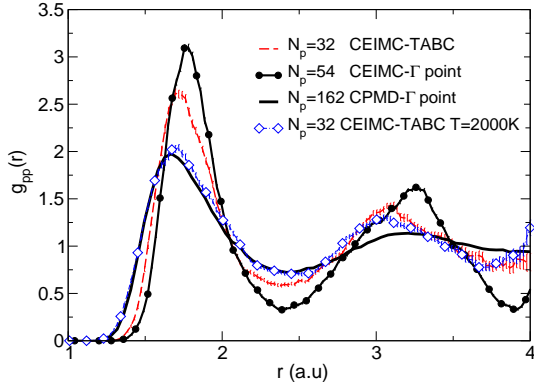


Fig. 1. Pair correlation function at $r_s = 1, T = 1000K$. Comparison between CEIMC-VMC-TABC with 32 protons, CEIMC-VMC-PBC with 54 protons and CPMD-LDA with 162 protons (simulation with $N_p = 54$ provides identical correlation). Data from CEIMC-VMC-TABC at $T=2000K$ (stars) are also reported.

Car-Parrinello molecular dynamics (CPMD) [9], the only difference is the method to calculate the potential energy surface. Whereas in CEIMC the Born-Oppenheimer energies are calculated by QMC methods, CPMD uses density functional theory (DFT) to calculate electronic energies. Both methods are in principle exact but rely on approximations of the unknown nodes of the trial wavefunctions in QMC and on the approximation of the unknown exchange-correlation energy functional in DFT. In Fig. 1 we compare the proton correlation function $g_{pp}(r)$ of both methods. The CEIMC results show more structure than CPMD of Ref. [9] using LDA. A better agreement is observed when CPMD results at temperature T are compared to CEIMC results at temperature $2T$ for $300 \leq T \leq 3000$. Already previous studies suggested that the Born-Oppenheimer energy surface from DFT-LDA is flatter than the more accurate one from QMC. In Ref. [8] differences in energy among various crystal structures obtained within LDA were found smaller than DMC energies by roughly a factor of two. Further, in Ref. [3,4], the energies for random configurations of molecular hydrogen showed more variation within DMC than LDA.

Note that the CEIMC curves of Fig. 1 are all obtained using VMC to obtain the electronic Born-Oppenheimer energies. RQMC requires roughly one order of magnitude more computer time than VMC. For this reasons large part of our results are based

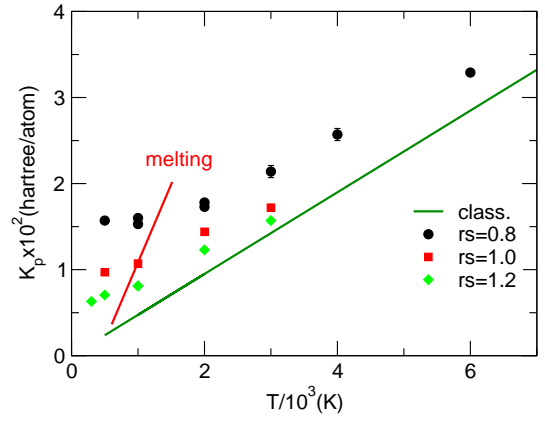


Fig. 2. CEIMC-VMC-TABC with 54 protons. Protonic kinetic energy per particle at various densities versus temperature. The red line estimates the melting of the bcc crystal from the Lindemann ratios.

on VMC calculation and RQMC is only exploited to estimate the systematic error of VMC. For the system with 54 protons at the Γ point, we have found no detectable differences in the correlation function between VMC and RQMC.

The Quantum effects of the protons The quantum effects of the protons are summarized in Fig. 2 which shows the kinetic energy of the protons versus temperature for three different densities ($r_s = 1.2, 1.0, 0.8$) and the deviation from its classical value $3k_B T/2$. Furthermore, Fig. 3 compares $g_{pp}(r)$ for a classical and a quantum calculation which directly shows that the zero point motion is extremely important. The quantum effects not only affect the proton kinetic energy but also increase the electronic energies and the configuration energy, at least at the variational level used in the present calculations.

Trial wave functions and zero temperature results In this subsection we discuss the zero temperature limit by VMC/DMC calculations at $T = 0$ of dynamical protons. In most of our CEIMC calculations, analytic trial wave functions including backflow and three-body correlation[14] for the electronic degrees

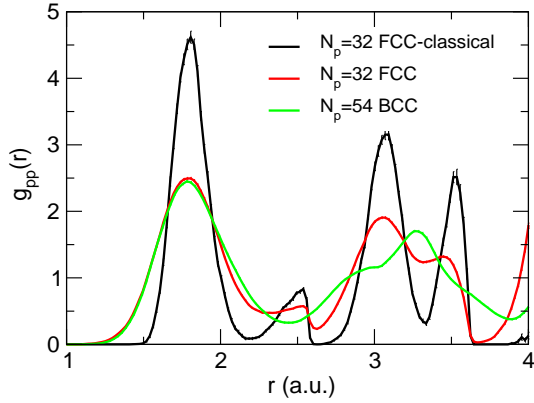


Fig. 3. Comparison of $g_{pp}(r)$ between classical and quantum protons at $r_s = 1$ and $T = 500K$ (CEIMC-VMC-TABC).

of freedom have been used. Here, we use this important ingredient of CEIMC to test their accuracy by comparing their energies for “dynamic” protons with the results of Natoli et al.[11] in the ground state using LDA trial wavefunctions. In these calculations, the LDA trial function was computed for a perfect bcc lattice and then modified for use within DMC calculations of moving protons in order to avoid recalculation of the LDA orbitals. In the present calculations, in addition to the backflow-threebody wavefunction for the electronic part of the wavefunction, the protonic part of the wavefunction contains a Jastrow correlation and has a Gaussian orbital localizing it to the bcc lattice sites (that was also in the Natoli calculation); exchange effects for protons due to statistics are neglected. In contrast to CEIMC, these DMC calculations do not make use of the Born-Oppenheimer approximation. From table 1 we see that the backflow wavefunctions have a lower energy by 2-3mH/atom within VMC and 2mH/atom within DMC. However, the analytical functions are particularly appropriate to our methods since their computational cost is much less than solving the Kohn-Sham equations for a random arrangement of 50 to 100 protons.

To extend the data of the equation of state of Ref. [5] to the zero temperature limit, we performed VMC-TABC calculations at zero temperature. The results are summarized in table 2. The zero point energy is obtained by subtracting the energy in a static bcc lattice of protons from the energy of the dynamic electron-proton system. In the harmonic approximation, half of the zero point energy will contribute to the potential

| N | wavefunction | E_v | σ^2 | E_{DMC} |
|----|--------------|--------------|------------|--------------|
| 16 | LDA | -0.4678 (2) | | |
| | BF-A | -0.4724(1) | 0.030 (2) | |
| 54 | LDA | -0.5195 (3) | | -0.52415 (5) |
| | BF-A | -0.52194 (5) | 0.025(1) | -0.52610(7) |

Table 1

VMC and DMC Energies in h/atom (and variance per electron σ) for dynamic protons and electrons at $r_s=1.31$ at $T = 0$. LDA means LDA orbitals times an optimized 1 body factor and Jastrow factor[8] used as trial wavefunction, BF-A are the analytical wavefunctions using backflow times an optimized gaussian for the protons.

| r_s | E_{tot} | E_{kin} | E_{pot} | P | ZPE | γ_L |
|-------|------------|-----------|-----------|----------|----------|------------|
| 0.8 | -0.0573(7) | 1.83(1) | -1.89(2) | 80(1) | 0.036(1) | 0.18(1) |
| 1.0 | -0.3477(6) | 1.208(2) | -1.556(2) | 20.02(6) | 0.023(1) | 0.150(2) |
| 1.2 | -0.4637(4) | 0.873(2) | -1.337(2) | 5.51(8) | 0.016(1) | 0.128(1) |

Table 2

Energies for 54 dynamic protons and electrons at $T = 0$ for various densities using VMC-TABC (averaged over 1000 twist angles); total (E_{tot}), kinetic (E_{kin}) and potential energies (E_{pot}) are given in h/at, P is the pressure in Mbar, ZPE the zero point energies and γ_L is the rms deviation divided by the nearest neighbor distance for a bcc lattice.

and the other half to the kinetic energy of the protons at zero temperature and we can compare with the protonic kinetic energies calculated in Ref. [5]. The zero temperature kinetic energies of the protons obtained is systematically higher than the zero temperature extrapolated results of Ref.[5]. It is known[7,8] that anharmonic effects are large for high pressure hydrogen. The difference could also be due to limitations of the gaussian trial wavefunctions for the protons used in the zero temperature VMC calculation. Indeed, in CEIMC, although electronic energies are calculated variationally, protons are represented by a path-integral; the CEIMC results are therefore more reliable.

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