Coupled Electron-Ion Monte Carlo Calculations of Dense Metallic Hydrogen

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We present an efficient new Monte Carlo method which couples path integrals for finite temperature protons with quantum Monte Carlo calculations for ground state electrons, and we apply it to metallic hydrogen for pressures beyond molecular dissociation. We report data for the equation of state for temperatures across the melting of the proton crystal. Our data exhibit more structure and higher melting temperatures of the proton crystal than do Car-Parrinello molecular dynamics results. This method fills the gap between high temperature electron-proton path integral and ground state diffusion Monte Carlo methods and should have wide applicability.

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The knowledge of the physical properties of hydrogen in a wide range of thermodynamic conditions is a key problem in planetary and high pressure physics [1,2]. In the search for the metallization transition, three different insulating molecular crystal phases have been clearly observed in diamond anvil cell experiments up to 3.2 Mbar [3] at room temperature and below. Metallization has been obtained in shock wave experiments for a warm dense molecular liquid [4], but properties at finite temperature and/or at higher pressure are largely unknown because experiments are difficult.

A large body of theoretical investigations of high pressure hydrogen [5] has helped the understanding of the experimental observations and hold out the prospect of predicting the room temperature metallization pressure and the phase diagram at higher pressure. However, the present understanding of high pressure hydrogen is unsatisfactory because energy differences among different crystalline phases are small requiring accurate total energy method to locate transition lines, size effects are large in metallic systems requiring Brillouin zone sampling, and proton quantum effects are important and can influence the energetic ordering of crystal phases. An accurate theoretical prediction of metallization may require accuracy beyond that of the (local-density approximation) LDA + GGA (generalized gradient approximation) density functional theory [6,7].

In this Letter, we describe a new quantum Monte Carlo (QMC) method. Previous QMC studies of hydrogen at $T = 0$ have treated electrons and protons at the same level of description and become inefficient in following the evolution of particles of very dissimilar mass ($m_p/m_e = 1836$). Nonetheless, they have established that pressure dissociation of hydrogen molecules at $T = 0$ K occurs at $r_s = [3/(4\pi n_e)]^{1/3} = 1.31$ ($P \sim 3$ Mbars) [8], where n_e is the electronic number density. Upon dissociation the molecular crystal transforms to a proton lattice of diamond structure and later to a lattice of cubic symmetry (bcc) at $P \geq 8$ Mbars [9]. Obviously, the interesting effects of temperature are absent in this procedure. At finite temperature, restricted path integral Monte Carlo (RPIMC) simulations [10] have been used to predict the equation of state (EOS) and to investigate the occurrence of the plasma phase transition [11]. In RPIMC simulations, both electrons and protons are at finite temperature, but it is efficient only for temperatures above 1/20 of the electronic Fermi temperature (roughly 3×10^4 K at $r_s = 1$). The new method described here, called coupled electronic-ionic Monte Carlo (CEIMC) method [12,13], is able to fill the gap between the RPIMC simulations and the ground state QMC methods. We study metallic hydrogen in a range of densities and temperatures where molecules are absent and where protons undergo a solid-fluid transition. We report results for the EOS and give a qualitative location of the transition line.

In the CEIMC method, in contrast to previous QMC methods, the electrons and protons are not treated at the same level but within the Born-Oppenheimer approximation. The proton degrees of freedom are advanced by a Metropolis algorithm in which the energy difference between a proton state S and a trial state S' is computed by a zero temperature QMC calculation [either variational (VMC) or reptation (RQMC) [14]] for the electrons. Unbiased sampling of the proton configurations is achieved using the penalty method [15] to take account of the statistical noise in the energy difference.

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 method) for the S and S' states, and we compute the energies for the two states as correlated sampling averages [12,13], thereby reducing the noise. Analytic trial wave functions, including backflow and three-body correlation [16], have been used. These functions are particularly appropriate since they are quite accurate without adjustable parameters requiring optimization and their computational cost

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is much less than using orbitals expanded in a plane wave basis as was done in previous QMC calculations [9].

To go beyond VMC level, we implemented a RQMC algorithm [14] to calculate, more accurately, the electronic ground state energy and other properties. Similar to diffusion Monte Carlo (DMC) method, in RQMC method the thermal density matrix projects out the ground state wave function from the trial function within the fixed-node approximation. This projection is accomplished by a Metropolis walk in path space. Because one has an explicit sampled distribution, it is easier to compute energy differences. Other quantities are computed without the mixed-estimator bias [14] of DMC calculations. The high quality of our trial wave functions makes it possible to relax to the ground state with a very limited number, P, of time slices. The electronic path space is sampled by a reptation algorithm in which, at each step, a new link is added to one end of the path and an existing link is deleted from the other end, subject to an acceptance/rejection test. In previous RQMC implementations, the growth direction was chosen at random. To speed up convergence we have introduced the "bounce" algorithm in which the growth direction is reversed only when a move is rejected [17]. The bounce algorithm can be shown to sample the correct probability distribution of the path and to explore phase space much more rapidly because the rejection probability is so low, typically less than 5%.

To reduce finite size effects in metallic systems, we used twist averaged boundary conditions (TABC) when computing electronic energies (i.e., we integrate over the Brillouin zone of the super cell) [13,18]. Using periodic boundary conditions (PBC) would require a system with more than 5000 electrons to reach the thermodynamic limit to the same accuracy. For a given protonic displacement, we compute the energy difference using only 100 electronic steps, but at 1000 different k points. After averaging over k points, the noise level is small enough to simulate temperatures as low as 100 K [13] for classical nuclei. This is an important feature of the CEIMC method: averaging over the boundary conditions does not make the calculation run much slower.

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 [19] of an effective proton-proton potential and treated the difference between the true Born-Oppenheimer energy and the effective potential with the primitive approximation. With this action, we find that a proton imaginary time step $\tau_p = 0.3 \times 10^{-3}\ \mathrm{K}^{-1}$ is appropriate for $r_s \geq 1$. We randomly assign a subset of k points (from the TABC) to each protonic slice. This does not cause a bias. The strategy allows one to simulate quantum protons at essentially the same computational cost as classical protons, except for the slower relaxation of the protonic paths. This is in contrast to a deterministic method such as *ab initio* path integral molecular dynamics [20] where the execution time per step would be multiplied by the number of protonic time slices *and* by the number of sampled k points.

In order to assess the accuracy of the CEIMC method, we first consider a system of $N_p = N_e = 16$ at $r_s = 1$ and $T = 5000$ K and compare with RPIMC calculations. CEIMC-RQMC calculations, performed with $\tau_e = 0.0125\ \mathrm{H}^{-1}$, $\beta_e = 0.5\ \mathrm{H}^{-1}$, lowers the VMC total energy by 4(2) mH/atom = 1260(630) K/atom. The VMC and RQMC pressures agree within error bars. Comparison between VMC and RQMC pair correlation functions is also very good (see Fig. 1). The $g_{pp}(r)$ RQMC curve is slightly more structured than the VMC one. RPIMC data, obtained with free particle nodes [10,13] and 1000 time slices, agree well with CEIMC ones. (Small differences in the $g_{ep}(r)$ are attributed to the more accurate nodal structure of CEIMC data compared to RPIMC data.)

Next we compare our results with Car-Parrinello molecular dynamics (CPMD) simulation [21] which uses the LDA computed forces. Figure 2 shows that CEIMC-VMC $g_{pp}(r)$'s exhibit considerably more structure than does LDA. CPMD simulations considered systems of classical protons at the Γ point only. We compare with two different CEIMC calculations for classical protons, namely, an open shell system ($N_p = 32$) with the TABC, and a closed shell system ($N_p = 54$) with the Γ point only. For the latter case, we find that the $g_{pp}(r)$ from VMC and RQMC calculations (not shown) agree; but they exhibit more structure than CPMD. The TABC one is in the liquid state, while the simulation using only the Γ point, initially prepared in a liquid state from temperature quenching, exhibits the onset of spontaneous crystallization. The

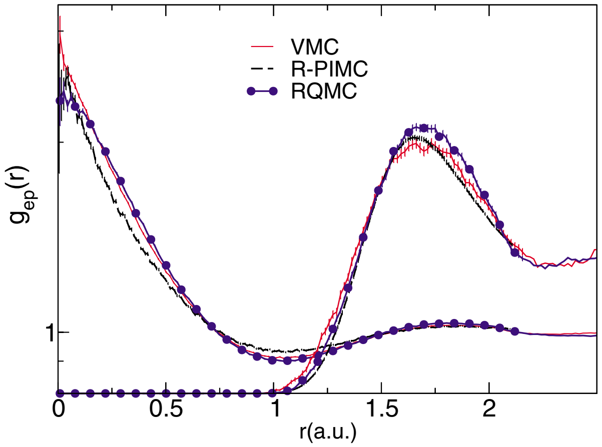

FIG. 1 (color online). CEIMC-RPIMC comparison for electron-proton and proton-proton correlation function at $r_s = 1$, $T = 5000$ K, $N_p = N_e = 16$.

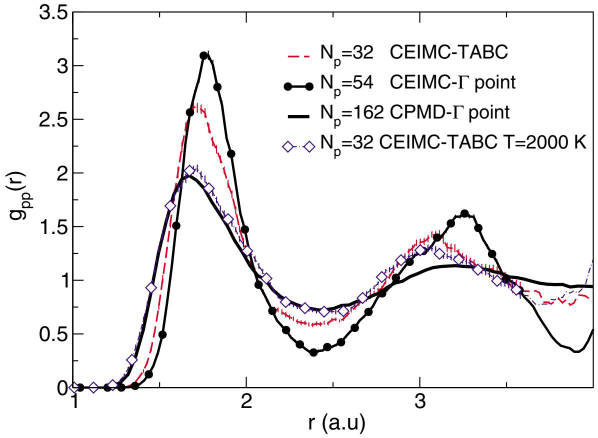

FIG. 2 (color online). Pair correlation function at $r_s = 1$, $T = 1000$ K. Comparison between CEIMC-VMC TABC with $N_p = 32$, CEIMC-VMC PBC $N_p = 54$, and CPMD LDA $N_p = 162$ (simulation with $N_p = 54$ is identical). Data from CEIMC-VMC TABC at $T = 2000$ K (◇) are also reported.

larger correlation in CEIMC results with respect to CPMD is compatible with our early estimate of the melting temperature of the fcc crystal of classical proton between 1000 and 1500 K [13] at variance with the LDA of 350 K (for the bcc crystal) [21]. The observed discrepancy between the CEIMC method and CPMD is surprising since LDA is generally believed to be accurate at high density. However, a previous study of hydrogen at $r_s = 1.31$ [9] reported that differences in energy among several crystal structures obtained within LDA are smaller than energy differences from DMC calculations by roughly a factor of 2. Also zero point energies in QMC calculations were roughly twice the LDA estimates (from the harmonic approximation). A study of liquid molecular hydrogen configurations [12] also found that DMC ground state energies fluctuate 40% more than the LDA energies do. This suggests that the Born-Oppenheimer surface from LDA is flatter than the more accurate one from QMC calculations. We have no comparisons with other density-functional theory (DFT) functionals. In addition, there is a known issue in computing the ionic temperature in CPMD simulations; the simple estimate based on the ionic kinetic energy provides only a lower bound of the true temperature [22]. Tracing the origin of the observed discrepancy between CEIMC and CPMD results would deserve an independent study. Here we just note that better agreement is observed between CPMD results at temperature T and CEIMC results at temperature $2T$ for $300 \leq T \leq 3000$; see for instance Fig. 2.

We have compared VMC results with the RQMC results at $r_s = 1.2$ and $T = 5000$ K. We find that the VMC energy is systematically higher by roughly 7.6(2) mH/atom = 2400(60) K/atom, while the VMC pressure is systematically lower by 0.03(1) Mbars. The error on the energy is expected to be independent of the temperature

TABLE I. Total energy, kinetic and potential energies, pressure, Lindemann ratio for bcc crystal, γ_L, and proton kinetic energy, K_p, for a system of $N_p = 54$ protons with VMC TABC. K_p can be compared to $3K_BT/2$ (last column). Units of energy are hartrees per proton. M_p is the number of protonic time slices ($M_p = 1$ means classical protons).

r_s	T(KK)	M_p	E	$E_{\rm kin}$	$E_{\rm pot}$	P(Mbars)	γ_L	$K_p \times 10^2$	$K_p^{cl} \times 10^2$
0.8	0.5	16	−0.0594(2)	1.8419(1)	−1.9033(1)	81.07(3)	0.169(1)	1.57(3)	0.2375
	1.0	16	−0.0586(4)	1.8428(4)	−1.9034(1)	81.16(3)	0.183(1)	1.53(4)	0.475
	2.0	8	−0.0522(4)	1.8338(4)	−1.9018(1)	81.69(3)		1.78(3)	0.950
	3.0	4	−0.0442(4)	1.8538(6)	−1.9000(2)	82.33(6)		2.14(7)	1.425
	4.0	4	−0.0382(8)	1.8590(8)	−1.8991(1)	82.83(6)		2.57(7)	1.900
	6.0	2	−0.0268(8)	1.8688(8)	−1.8974(2)	83.80(6)		3.29(4)	2.850
	10.0	1	0.016(1)	1.8886(8)	−1.8934(4)	85.78(9)		4.750	4.750
1.0	0.5	8	−0.3512(2)	1.2142(2)	−1.5655(1)	20.101(3)	0.177(1)	0.97(2)	0.2375
	1.0	4	−0.3480(2)	1.2176(2)	−1.5657(1)	19.68(1)		1.07(2)	0.475
	2.0	4	−0.3430(2)	1.2260(4)	−1.5653(1)	20.65(1)		1.44(2)	0.950
	3.0	2	−0.3356(4)	1.2298(4)	−1.5655(1)	20.83(1)		1.72(3)	1.425
	5.0	1	−0.3262(6)	1.2390(6)	−1.5652(1)	21.26(2)		2.375	2.375
	10.0	1	−0.2888(6)	1.2740(4)	−1.5630(2)	22.95(3)		4.750	4.750
1.2	0.3	10	−0.46610(4)	0.8776(1)	−1.3437(1)	5.554(1)	0.134(1)	0.59(1)	0.1425
	0.5	8	−0.4661(1)	0.8792(1)	−1.3439(1)	5.594(3)	0.177(2)	0.67(1)	0.2375
	1.0	4	−0.4632(1)	0.8811(2)	−1.3443(2)	5.641(3)	0.196(3)	0.77(1)	0.475
	1.0	4	−0.4610(2)	0.8858(2)	−1.3468(1)	5.735(6)	Liquid	0.77(1)	0.475
	2.0	4	−0.4552(2)	0.8918(2)	−1.3469(1)	5.893(6)		1.19(3)	0.950
	3.0	2	−0.4492(4)	0.8996(3)	−1.3488(1)	6.08(2)		1.53(3)	1.425
	5.0	1	−0.4386(6)	0.9106(4)	−1.3492(2)	6.37(2)		2.375	2.375
	10.0	1	−0.4036(6)	0.9478(4)	−1.3514(1)	7.34(2)		4.750	4.750

and to decrease with increasing density. Even though the amount of energy missing in VMC calculations is quite large on the proton energy scale, we observe only a minor effect on $g_{pp}(r)$; energy differences are quite accurate within VMC calculations. On the basis of the above results, we performed a VMC study of the EOS and report the results in Table I. (RQMC calculation is roughly an order of magnitude more expensive than VMC calculation.)

The zero point proton motion affects not only the proton kinetic energy but also increases the electronic kinetic energy and, to a smaller extent, the configurational energy. At $r_s = 1$ and $T = 500$ K, we find a total energy increase of 14.9(2) mH/atom = 4670(60) K/atom, of which 2020(30) K/atom comes from the proton kinetic energy, 2200(20) K/atom the electronic kinetic energy, and 450(10) K/atom the configurational energy. Residual finite size effects have been estimated from static lattice calculation at $r_s = 1$ to be of the order of 10 mH/atom on the energy, and 0.2 Mbars on the pressure. The transition line, estimated by the dynamical observation of melting, is located between 1000 and 2000 K at $r_s = 0.8$, between 500 and 1000 K at $r_s = 1.0$, and close to 1000 K at $r_s = 1.2$. Indeed, at the latter density and at $T = 1000$ K, the system is able to sustain both liquid and crystal states for the entire length of our simulations (80 000 protonic steps).

In conclusion, we have developed a new and efficient QMC method to study low temperature quantum protons and ground state electrons, which is a major improvement over previous QMC and DFT-LDA based methods. It allows for simulations of many-body hydrogen using QMC calculations for the electronic energies. We have developed efficient procedures to include protonic path integrals and k-point sampling. We have applied it to metallic hydrogen and investigated the solid-fluid transition of the protons. The present methodology can be extended in several ways. Constant pressure algorithm would be useful to study structural phase transitions. The method can be easily extended to the insulating molecular phase by replacing the metallic trial functions with localized molecular orbitals [12,13]. A study of the melting line of molecular hydrogen is in progress. Consideration of the metal-insulator transition requires a trial function that goes smoothly from metallic to localized orbitals. We are investigating an accurate and efficient form for this. Extension of the present method to more complex elements is straightforward, provided we have efficient trial functions.

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