Crystal Structure of Atomic Hydrogen

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We have performed quantum Monte Carlo calculations on atomic metallic hydrogen at zero temperature and constant volume (r_s=1.31) for protons rigidly fixed to lattice sites and for protons having zero point motion. By studying a variety of crystal structures including bcc, simple cubic, simple hexagonal, diamond, and β-Sn, we show that low-coordination structures, especially diamond, are energetically favored for a range of pressures around 3.0 Mbars. Our results show that it is essential to treat the electrons beyond the local density approximation and protons beyond the harmonic approximation to predict the correct ground state structure.

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It was first pointed out by Wigner and Huntington [1] that at sufficiently high pressures, hydrogen should dissociate from its molecular state to form a metal. Metallic hydrogen has been the focus of much theoretical and experimental work [2] because of its special role as the simplest of all metals, its importance in the evolution and composition of heavy planets, and the expectations of high temperature superconductivity [3,4]. Although the structure of metallic hydrogen is fundamental to understanding these properties, there is no consensus on even the most basic aspects. Though Wigner and Huntington studied the possibility of transformation to the atomic bcc lattice only, they suggested the possibility that a less symmetric lattice may be preferred by drawing analogies with allotropic modifications of other elements. Subsequent work has led to diverse predictions, with many studies supporting low-coordination anisotropic structures [5–8], others concluding that high-coordination isotropic structures are favored [9,10], and yet others considering the possibility of a quantum liquid state [11]. The main reason for these differences lies in the difficulty in treating the large zero point motion of the protons and the effect of electronic correlation near the atomic-molecular transition.

We carry out diffusion quantum Monte Carlo (QMC) calculations including both electrons and protons as quantum particles, to compare the energies and pressures of hydrogen in characteristic low and high symmetry structures. The methods are close to those of Ceperley and Alder [9]. However, we have made improvements described below which are crucial for accurate QMC calculations on low-coordination structures. Since our methods use local density calculations as the first step, we are able to compare directly with other recent calculations which have primarily used that approximation [5,12,13]. We show that it is necessary to treat the proton motion accurately, including anharmonicity, to predict the correct ordering of the structures, and that the combined effects of electronic bonding and proton motion stabilize a family of structures not considered before.

The methods we used to calculate the total energy of the ground state of hydrogen were variational Monte Carlo (VMC) and fixed-node diffusion Monte Carlo (DMC). The VMC technique estimates the variational energy of an assumed trial wave function, and DMC projects out an improved ground state from the trial wave function by simulating a branching random walk [9,14]. DMC gives the exact ground state energy for bosons and distinguishable particles and the best possible upper bound for fermions within the fixed-node approximation [9,14]. Since exchange effects between protons are negligible, the only essential approximation in our work is the nodal surface of the electrons.

Consider first the electronic wave function with protons fixed at positions $\{R\}$. The static many-body trial wave function we used is of the Slater-Jastrow form, which is the product of symmetric and antisymmetric terms,

$$\Psi(\{r\},\{R\}) = \exp\left[-\sum_{i\neq j} u_{ee}(r_i - r_j) - \sum_{iJ} u_{ep}(r_i - R_J)\right] D^{\uparrow}\{\phi_k(r_l)\}\, D^{\downarrow}\{\phi_k(r_l)\}\,, \tag{1}$$

where u_{ee} and u_{ep} are the electron-electron and electron-proton correlation functions, respectively. These pair correlation functions, derived within the random phase approximation (RPA) [15], were found to work well for the electron gas [15] and in previous work done on hydrogen [9]. They contain both the exact small r (cusp conditions) and large r (plasmon) behavior. $D^{\uparrow}$ and $D^{\downarrow}$ are Slater determinants of the single-body wave functions ϕ_k for spin-up and spin-down electrons.

In the Monte Carlo calculations of Ceperley and Alder [9], the single-body wave functions $\phi_k(r_l)$ were taken as plane waves $e^{i\mathbf{k}\cdot\mathbf{r}_l}$ with $|\mathbf{k}| < k_f$. Here, the single-body wave functions used are the self-consistent solutions to the Kohn-Sham equations in the local density approximation (LDA), as was done in a previous VMC study of bcc hydrogen [16]. These functions may be represented as

$$\phi_{k_l}(r_m) = \sum_G c_{Gk_l} e^{i(\mathbf{k}_l+\mathbf{G})\cdot\mathbf{r}_m}, \qquad (2)$$

where **G** are the reciprocal lattice vectors of the unit cell. Since the LDA wave functions include electron-proton correlations, the electron-proton pair potential term in Eq. (1) is modified [17]. In addition, the occupied orbitals are taken to be those given by LDA, which are different from the spherical distribution used previously. Improvement in the trial function is important because it allows more rapid convergence of the diffusion calculation and because the nodes of the wave function are determined by the Slater determinant and are not improved by the fixed-node DMC method. For example, using plane waves for the single-body wave functions, Ceperley and Alder found that the variational energy of the static bcc lattice with 128 atoms at $r_s = 1.31$ is $-0.957(1)$ Ry and the diffusion energy is $-0.992(1)$ Ry, whereas we find $-0.9924(4)$ Ry and $-0.9955(4)$ Ry, respectively. This is typical of the improvement in energy. We estimate the fixed-node error in the present DMC results to be approximately 0.5 mRy/atom for the static lattice and 1.5 mRy/atom for the dynamic lattice. This is based on results of released node calculations on the homogeneous electron gas [18] which found the error is roughly $0.1(E_{\text{VMC}} - E_{\text{DMC}})$ and is supported by our comparison with the plane wave results above.

In the case of the dynamic lattice, there are additional protonic terms in the trial wave function Eq. (1), namely, a proton-proton correlation function u_{pp}, also derived within the RPA [15], and a product of Gaussian orbitals centered on lattice sites. The size of these Gaussian orbitals is used as a variational parameter. In solid ^{3}He, exchange contributions to the energy are very small (typically less than 10^{-4} of the kinetic energy [19]). Our tests show that this is also true in the case of solid hydrogen. For this reason it is an excellent approximation to treat protons as distinguishable particles and speed up the calculation by not introducing another set of Slater determinants to the trial wave function.

Since the occupied **k** states of the single-body wave functions change with the size and shape of the periodic cell, it is essential to carefully extrapolate our calculations for systems of finite size to get a result applicable to the infinite system. This is particularly important in a metal because the delocalized electronic wave functions are sensitive to the boundary conditions. For each separate crystal structure we fit [9] our finite size calculations which range from 8 to 432 atoms to

$$E_N = E_\infty + c_1\left(E_\infty^{\text{LDA}} - E_N^{\text{LDA}}\right) + \frac{c_2}{N} \qquad (3)$$

by varying E_∞, c_1, and c_2. Good quality fits are obtained in all cases, thus justifying the approach. For β-Sn and simple hexagonal we used optimal LDA c/a ratio, of 0.9129 and 0.6, respectively.

The statistical errors for all calculations were found to be <1 mRy/atom. In addition to the fixed-node errors, there are other systematic errors which arise from the finite time step. Ceperley and Alder estimate the time step error to be on the order of 1 mRy/atom by comparing their diffusion results with results using Green's function Monte Carlo calculations.

Table I shows the results of our total energy calculations on the static and dynamic lattice. For the static lattice, VMC gives energy differences between structures in excellent agreement with the DMC results while LDA does not. Since the difference in energy between E_{VMC} and E_{DMC} is a measure of the quality of the variational

TABLE I. The static and dynamic LDA, VMC, and DMC energies, for the different crystal structures. Also shown are the zero point energy, virial pressure, and Lindemann's ratio.

	E_{LDA} (Ry)	E_{VMC} (Ry)	E_{DMC} (Ry)	E_{ZPE} (Ry)	P (Mbar)	γ
			Static			
bcc	−1.01392	−1.0062(3)	−1.0101(3)		2.53(4)	
Simple cubic	−1.01898	−1.0144(4)	−1.0185(3)		2.85(3)	
Simple hexagonal	−1.02406	−1.0275(4)	−1.032(1)		3.30(2)	
Diamond	−1.02413	−1.0204(4)	−1.0235(2)		3.27(4)	
β-Sn	−1.02711	−1.022(1)	−1.0256(7)		2.89(4)	
			Dynamic			
bcc		−0.9716(1)	−0.9810(7)	0.0291(7)	2.89(3)	0.12
Simple cubic		−0.9747(1)	−0.9873(3)	0.0312(3)	3.11(2)	0.11
Simple hexagonal		−0.9828(2)	−0.988(1)	0.044(1)	3.54(1)	0.17
Diamond		−0.9821(2)	−0.993(1)	0.0305(1)	3.47(4)	0.18
β-Sn		−0.981(1)	−0.992(2)	0.036(2)	3.33(9)	0.16

wave function, it is apparent that the accuracy is comparable in all the static structures. However, we see that full DMC calculations are needed to establish the dynamic crystal structure of atomic hydrogen at this density since VMC makes errors as large as 13 mRy/atom.

Our results for the static lattice indicate that the simple hexagonal lattice is the most stable at this density and that in general, anisotropic structures with lower coordination are preferred. The preference for anisotropic structures by metallic hydrogen at this density in the static limit has been well documented by both perturbation theory calculations [6,7] and LDA [5]. The tendency toward anisotropy is surprising because of the simple interactions in this problem, but it can be understood by considering the structure-dependent part of the electron energy. Since hydrogen has no inner shell, the Fourier representation of the electron-ion interaction has the same sign over the whole reciprocal lattice. When this is the case, it is possible to show [6,7], using second-order perturbation theory, that the energy is lowered by forming anisotropic structures which have small magnitudes for the first few reciprocal lattice vectors. At higher densities the Madelung contribution, which scales like r_s^{-1}, dominates and is optimized by close-packed structures like bcc.

The zero point motion in this problem is extremely important. Its magnitude is larger than the differences in static energies discussed above, and it has been proposed by Straus and Ashcroft [10] that the dependence on structure will be great enough to ultimately favor isotropic structures. A proper treatment of the lattice degrees of freedom is critical to obtaining accurate results for the real crystal. Since the protons and electrons equilibrate on very different time scales, including protonic degrees of freedom slows the convergence by a factor of about 10. To avoid many costly calculations, one DMC calculation was done on a moderately sized system (≈ 60 atoms) for each structure and the result was extrapolated to the infinite bulk using the VMC fitting parameters. Note that the VMC and DMC fitting coefficients for the static lattice are the same to within a few percent.

Table I shows the results of our VMC and DMC calculations on the dynamic lattice. We define the zero point energy (ZPE) to be the difference between the static and dynamic diffusion energies. For these structures, in general, lower coordination leads to higher ZPE as was discussed by Straus and Ashcroft [10] and Ceperley and Alder [9]. Diamond, however, has among the lowest ZPE so that its final energy, including all contributions, is lowest of all the structures considered. Brovman, Kagan, and Kholas [6] studied the diamond lattice and associated it with a "quartic family" of structures which includes β-Sn. While they found this family energetically favored in the static limit, their calculations find a large zero point energy contribution which raises their total energy above that of the primitive hexagonal structure. Also presented is the pressure, calculated from the virial, and Lindemann's ratio γ, defined as the ratio of the rms displacement to the nearest neighbor distance. The table indicates that γ is ≤ 0.2 which is below the value of ≈ 0.3 associated with quantum melting [20].

One is struck by the fact that, where a comparison can be made, our calculated ZPE is larger by as much as a factor of 2 than that of Barbee *et al.* [5], and Brovman, Kagan, and Kholas [6] who estimated the ZPE by a set of phonon frequencies at a few points in the Brillouin zone and assumed the harmonic approximation ZPE$=\frac{1}{2}\hbar\langle\omega\rangle$. We believe that the difference is due to the anharmonicity of the proton motion. Our studies using the LDA show that the energy surface is typically shallow near the lattice sites but rises steeply, in a decidedly anharmonic fashion if the atoms are displaced too far from their lattice sites.

To determine the ground state structure, we show in Fig. 1 a plot of the difference in enthalpy ($E+PV$) from bcc versus pressure for the five structures. The values and slopes at the points indicated are derived directly from the DMC energies and pressures calculated at $r_s = 1.31$. To generate energy and pressure at other densities, we calculate the changes in electronic energy using LDA and the changes in the ZPE by fitting previous DMC results [9] to the expression $a_0 r_s^{-3/2} + a_1 r_s^{-1/2} + a_2 r_s^{1/2}$ suggested by Kagan, Pushkarev, and Kholas [21]. Our calculations indicate that in the range of pressures around 3 Mbars where the transition from a molecular solid to an atomic solid is postulated to occur [9], the diamond structure is favored over the others considered. Our extrapolations predict that with increasing pressure, atomic hydrogen will undergo the sequence of transformations diamond → β-Sn → sc → bcc. However, the results for β-Sn and diamond are within error bars and we have not

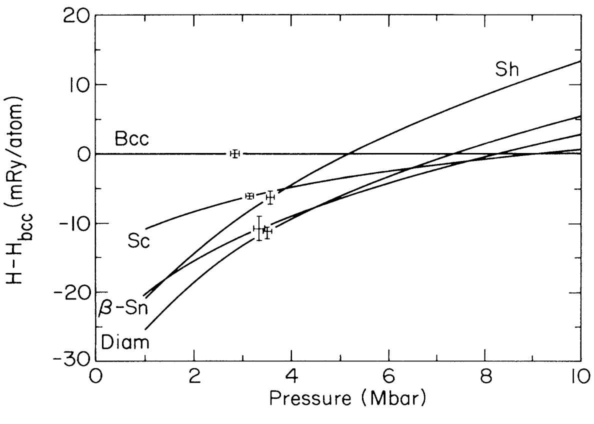

FIG. 1. Enthalpy difference from bcc vs pressure for the five dynamic crystal structures considered. The points with error boxes are derived from the DMC calculations done at $r_s = 1.31$ and the lines indicate extensions to other densities using the LDA and a functional form for the zero point energy as described in the text. Molecular structures not considered here are stable at pressures below approximately 3 Mbars.

considered other possible structures. Our results suggest a rich phase diagram as a function of temperature, since the energies are so close at $T = 0$, and the different vibrational energies lead to different entropies at $T > 0$. In addition deuterium may be expected to behave very differently.

To summarize, we have carried out extensive calculations of energy and pressure for five different crystal structures of hydrogen at the density $r_s = 1.31$, where an atomic structure is expected to be stable. We find that anisotropic structures are favored in the static limit, in agreement with previous work which used perturbation theory and the LDA [5–7]. In addition, the large zero point motion of the protons favors symmetric structures, as previously found by Straus and Ashcroft [10] as well as by Ceperley and Alder [9]. The combination of these effects leads to the most favorable structure being diamond, which has the lowest possible coordination of any highly symmetric three-dimensional structure. We conclude that for a range of pressures near 3.5 Mbars, hydrogen will form a low-coordination structure like diamond, and higher coordination structures will occur only with increasing pressure. Further studies of the properties of hydrogen are planned.

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