

Crystal Structure of Molecular Hydrogen at High Pressure

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We have studied oriented phases of molecular hydrogen on the hcp lattice using quantum Monte Carlo methods, treating both electrons and protons as quantum particles. We find that for a wide range of pressures above approximately 123 GPa ($r_s = 1.57$), structures with molecules at an angle to the c axis are favored over the structure with molecules aligned along the c axis. For pressures greater than 150 GPa, where phase III is observed, the most stable structures which we have found are insulating, with molecules having an average orientation angle of 60° with respect to the c axis. This conclusion is consistent with recent observations of strong ir activity, which is forbidden in the aligned structure. Consequences for the phase diagram are discussed.

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Experiments on solid molecular hydrogen and deuterium at high pressure [1–5] have revealed phase transitions that may include a metallic molecular state [3,4,6,7]. The transition to phase III near 150 GPa is marked by a discontinuous drop in the Raman active vibron mode [1,8] and a 3 order of magnitude increase in the vibron infrared activity [9,10]. The structure of this high pressure phase is crucial for interpreting the experimental results and resolving the issue of whether phase III is metallic. In this Letter we report the results of a quantum Monte Carlo study of the structure and properties of the molecular phase of solid hydrogen at high pressure. In combination with group theoretical analysis of the experimental results [11–13] our quantitative calculations provide strong evidence that phase III is insulating. These results also provide important new insights relevant to the overall phase diagram.

At low pressures, solid molecular hydrogen is known through direct x-ray diffraction measurements [14] to be an insulating hexagonal close-packed solid with molecules freely rotating on hcp sites. Experimental difficulties, primarily due to the vanishingly small sample size, have thus far prevented a direct determination of the crystal structure at higher pressures. Nevertheless, based upon acoustic phonon spectra [15], it is believed that the molecules remain centered on hcp lattice sites up to and through the phase III transition. The search for the lowest energy structure may therefore be reasonably restricted to differently oriented molecules centered on hcp sites.

Theoretical work has suggested that the question of metallic vs insulating behavior hinges upon the molecular orientation. In particular, band-overlap induced metallization occurs most readily if the molecules are aligned along the c axis [16,17], the structure first proposed by Abrikosov [18] and which we will refer to as mhcp- c . The best theoretical calculations using the local density approximation (LDA) plus corrections [17] and many-body “GW” self-energy calculations [19] find that metallization in mhcp- c occurs at 150 GPa. This is intriguingly close to the pres-

sure of the phase III transition where evidence for possible metallization has been reported [3,4,6,7]. Alternatively, freely rotating molecules and more complicated orientations, such as the low-energy structures proposed by Kaxiras and co-workers [20–22], have larger band gaps and consequently higher predicted metallization pressures.

Prior theoretical attempts to determine the structure of the solid molecular phase have relied primarily on density functional theory in the LDA. Calculations by Barbee *et al.* [23], for example, find mhcp- c to be energetically favored near the 150 GPa transition. These calculations included zero point energy by summing harmonic modes over the Brillouin zone. Surh, Barbee, and Mailhot [24] argue that the zero point energy will be further lowered in the mhcp- c structure because of reductions in phonon frequencies upon metallization. On the other hand, Kaxiras, Broughton, and Hemley [20], also using LDA methods, find more complicated “herringbone” orientations to have lower energy with larger gaps that close at pressures above 250 GPa. Furthermore, Nagara and Nakamura [25] find the lowest energy molecular structure to have the space group $Pca2_1$, a structure which is similar to Kaxiras’s herringbone but with a larger unit cell. However, none of the work on these lower symmetry structures has explicitly considered the effects of zero point energy. The best estimates of zero point energy have been reported by Ceperley and Alder [26] using quantum Monte Carlo calculations to study several different cubic based molecular structures. They did not consider any candidates based on the hcp lattice. Thus the present state of theoretical development on solid molecular hydrogen falls into two groups: one whose work suggests phase III to be mhcp- c and metallic [23,24], with a possibly crucial role played by zero point motion, and another that suggests that phase III has a more complicated orientation and remains insulating [12,20–22,25].

To clarify these disparate positions we have performed variational and diffusion Monte Carlo (VMC and DMC)

calculations on the oriented phase of molecular hydrogen at several different densities which include phases I, II (also referred to as the broken symmetry phase or BSP), and III (also referred to as H-A). In VMC, observables are estimated by the statistical evaluation of their expectation values with a trial wave function. In DMC, the imaginary time Schrödinger equation is solved with a statistical process of diffusion and branching of system ensembles that results in the sampling of the exact ground state for bosons and a much better variational upper bound in the case of fermions. An important advantage of the Monte Carlo approach is its ability to treat protons as dynamic quantum particles including anharmonic effects. We determine an accurate estimate of the zero point energy by comparing with static calculations in which the protons are treated as fixed particles.

Methods and procedures presented here are similar to those used for our study of hydrogen in the nonmolecular phase [27] and by Ceperley and Alder [26] in their molecular study. The trial wave function comprises an antisymmetric Slater determinant of single-body Kohn-Sham wave functions, taken from a density functional calculation using the LDA, and symmetric pair correlation functions. The electron-electron and electron-proton pair functions were derived by minimizing energy within the random phase approximation framework. These pair functions gave good results for the electron gas and for the atomic phase of hydrogen. The proton-proton correlation functions were those previously used by Ceperley and Alder [26]. Although the LDA single-body wave functions were calculated for a fixed static configuration of the protons, they were still very effective in the dynamic atomic calculations because the trial function is modified [27] to ensure that the cusp moves along with the protons. For nonmolecular structures this provided a significant improvement over the best prior Monte Carlo results. As long as the zero point motion of the molecules allows them to remain close to the sites where the wave functions were calculated, we find this approach to be equally successful in the present work [28].

To find the optimal static orientation of the molecules on the hcp lattice, we calculated the energy of a series of differently canted structures. The minimum energy configuration of the hcp basis has molecules canted in opposite directions at an angle of 60° with respect to the c axis at $r_s = 1.45$ and $r_s = 1.31$ [see Fig. 3(e) in Ref. [21]]. The optimized structure, henceforth designated mhcp- o , is about 7 mRy/atom lower in energy than mhcp- c at $r_s = 1.45$ ($P = 200$ GPa). These results are in general agreement with those of Kaxiras and Broughton [21], who found the optimum polar angle close to 60° , however, our energy gain compared to mhcp- c is significantly larger. The $Pca2_1$ structure [25] was not investigated because the larger unit cell would make the calculations too lengthy and the LDA calculations show an energy drop of less than 1 mRy per atom.

The main study of static and dynamic structures compared mhcp- c with mhcp- o , using LDA, VMC, and DMC. Calculations were done on a system of 48 molecules at $r_s = 1.31, 1.45,$ and 1.77 with $c/a = 1.58$. The energy was minimized with respect to all variational terms in the trial wave function including one parameter that determines the degree of orientation. The most significant conclusion of this study is that for a wide range of pressure, the mhcp- o structure is strongly preferred over mhcp- c . The main reason is the difference in static structural energy; the zero point energy being roughly the same for both, especially at high pressure. As may be seen in Table I the dynamic diffusion energy of mhcp- c is lower by 2 mRy/atom at $r_s = 1.77$, whereas mhcp- o is favored by 5 mRy/atom at $r_s = 1.45$, increasing to 14 mRy/atom at $r_s = 1.31$. These energy differences support the formation of the canted structures for r_s less than approximately 1.57, i.e., at any pressure above approximately 123 GPa. This would include part of phase II and the phase III region of the hydrogen phase diagram.

As demonstrated in our previous study of atomic structures, size effects can be particularly severe in metallic systems. To assess the magnitude of the correction due to size effects, several representative calculations were done for a system of 96 molecules. The results of these calculations leave our conclusions unchanged for $r_s \geq 1.45$ which includes phase II and a significant part of phase III.

Figure 1 compares the dynamic diffusion energy vs r_s for mhcp- o , mhcp- c , an extrapolated equation of state from Hemley *et al.* [29], the lowest energy nonmolecular structure, atomic diamond [27], and the energies of

TABLE I. LDA, variational, and diffusion Monte Carlo energies for mhcp- c and mhcp- o oriented molecular structures on an hcp lattice at three densities. Energy is given in Ry/atom.

		LDA		
Static	mhcp- c	-0.983	-1.047	-1.109
	mhcp- o	-0.992	-1.054	-1.111
		Variational		
		$r_s = 1.31$	$r_s = 1.45$	$r_s = 1.77$
Static	mhcp- c	-1.007(1)	-1.0833(1)	-1.144(1)
	mhcp- o	-1.0212(1)	-1.0859(5)	-1.1486(5)
Dynamic	mhcp- c	-0.961(1)	-1.025(1)	-1.113(1)
	mhcp- o	-0.976(1)	-1.045(1)	-1.113(1)
zpe	mhcp- c	0.046(1)	0.052(1)	0.031(1)
	mhcp- o	0.045(1)	0.040(1)	0.035(1)
		Diffusion		
		$r_s = 1.31$	$r_s = 1.45$	$r_s = 1.77$
Static	mhcp- c	-1.0130(2)	-1.0836(2)	-1.1524(2)
	mhcp- o	-1.0262(2)	-1.0902(2)	-1.1546(2)
Dynamic	mhcp- c	-0.9673(3)	-1.0454(3)	-1.1238(3)
	mhcp- o	-0.9812(2)	-1.0503(3)	-1.1215(3)
zpe	mhcp- c	0.045(1)	0.038(1)	0.028(1)
	mhcp- o	0.045(1)	0.039(1)	0.033(1)

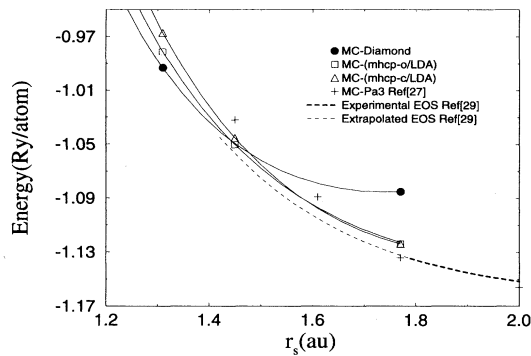


FIG. 1. Equation of state as determined by DMC calculations on two orientations of molecular hcp hydrogen compared with an equation of state extrapolated from experiment due to Hemley *et al.* [29]. Monte Carlo results for diamond [27] and *Pa3* [26] are also presented.

Ceperley and Alder [26] for *Pa3*. In Ref. [20], Kaxiras, Broughton, and Hemley calculate the energy difference between *mhcp-c* and *mhcp-o*. Their numbers indicate that the energy difference peaks near $r_s = 1.5$ and then stays fairly constant out to higher pressures. Our results show a larger energy difference which continues to grow with increasing density. More complicated orientations such as *Pca2₁* [25] may be stabilized further. Comparison with Ceperley and Alder's data on *Pa3* demonstrates the importance of the improved trial wave function and the optimized structure. Since Ref. [26] used a trial wave function which more accurately describes freely rotating molecules, it provides a better result at low pressure ($r_s = 1.77$) than the oriented wave functions used here. Freely rotating molecules on the hcp lattice are, in fact, the lowest energy configuration for low pressure [28]. A tangent construction connecting the lowest energy molecular structure, *mhcp-o*, and the lowest energy atomic structure, diamond, indicates a transition pressure of 230 ± 25 GPa, a result lower than that found by Ceperley and Alder [26]. However, we believe it is likely that the actual transition will be higher, because our molecular phase is not as well optimized as the atomic phase. Other more stable molecular structures, such as *Pca2₁*, would be expected to increase the transition pressure.

Our principal finding that canted molecular structures such as *mhcp-o* are more stable than the *c* axis aligned structure *mhcp-c* in both phases II and III is supported by recent observations of infrared active vibrational modes in these phases [9,10]. As Zallen, Martin, and Natoli [13] have demonstrated, all structures with two or more molecules per cell must have ir active modes of vibration, with the exception of two hexagonal structures, one of which is *mhcp-c*. This is consistent with the fact that no first order ir activity is observed in phase I, which has rotating molecules and the same symmetry as *mhcp-c*. The appearance of ir activity in phases II and III is

inconsistent with *mhcp-c*, but consistent with any of the canted *mhcp-o* type structures. In addition, the fact that hydrogen and deuterium have similar pressures for the phase III transitions [10,30] is in general agreement with our conclusions that the zero point energy does not change markedly as a function of the orientation and does not drive the transition.

One of the consequences of the symmetry considerations for the phase diagram [11,12] is that there must be a boundary separating phase I from phases II and III as a function of pressure and temperature. It has been established [10,30] in deuterium that phase II terminates in a triple point, and at higher temperatures the boundary is between phases I and III. It seems likely [10,30] that similar behavior occurs in hydrogen. This boundary can be first or second order and it may change from first to second order at a tricritical point. However, it cannot terminate in a simple critical point, as was proposed based upon the observation that the first order jump in Raman frequencies becomes continuous at high T [5,6].

There are also two clear alternatives for the phase diagram at yet higher pressures. Lonsdaleite, (sometimes referred to as "hex diamond") is a structure which is easily reached from *mhcp-c* by stretching the molecular bond until each proton has four equidistant neighbors. If hydrogen forms the lonsdaleite structure, then the phase diagram could have the form shown in Fig. 2(a) where the low-symmetry oriented phases are completely enclosed by the region with full hexagonal symmetry. Lonsdaleite, which has hcp symmetry could be connected to phase I by a continuous path, i.e., not separated by a phase line. This would imply that the phase III transition line curves over and intersects the $T = 0$ axis again at the point of the $T = 0$ molecular-atomic transition. A further transition from lonsdaleite to a structure with cubic symmetry would be first order and separated by a phase boundary. Alternatively, there could be a first-order transition from phase III to a cubic phase (such as diamond) as shown in Fig. 2(b).

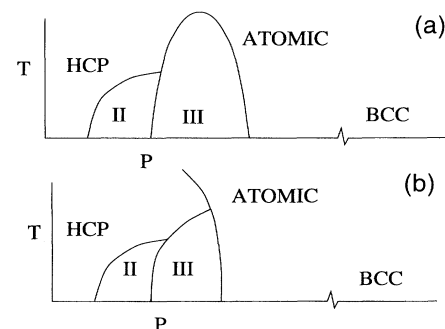


FIG. 2. Schematic figures of possible phase diagrams of solid hydrogen. (a) Atomic structure with hcp symmetry, e.g., lonsdaleite; (b) Atomic structure with cubic symmetry, e.g., diamond. A sequence of transitions to more close-packed structures leading to bcc is expected at higher pressures [27].

The main result of our molecular study is that we find insulating canted orientations of molecules on the hcp lattice of the type proposed in Ref. [20] to be favored over the mhcp-*c* orientation for a range of high densities beginning at $r_s = 1.57$. This includes the region of phase II or BSP and phase III or H-A. Specifically we have concentrated on an optimized orientation that was first suggested by Kaxiras, Broughton, and Hemley [20], and which we have called mhcp-*o*. Our energy differences including zero point motion are even larger than those found by the static LDA calculations [21], and they support the conclusion that these insulating orientations persist into phase III of the hydrogen phase diagram. Furthermore, our Monte Carlo calculations independently find that hydrogen in these structures is indeed insulating, since the minimum energy was found with insulating occupations of the trial Monte Carlo state. Thus we do not expect the mhcp-*c* structure, which has the smallest gap of all orientations [16], to be a stable phase in phase III. A transition to mhcp-*o* or other low-symmetry insulating structures as our results suggest, would activate ir vibrational modes and is supported by the observation of increased ir absorption beyond the phase III transition [9,10].

A generalization which emerges from extensive calculations on both atomic and molecular phases is that solid hydrogen tends to form low-symmetry, low-coordination structures which exhibit insulating gaps as found for the molecular structures considered here, or semimetallic behavior which is expected for the diamond and lonsdaleite structures found in our previous work on nonmolecular phases [27]. In the oriented molecular phases, where we find that zero point energy does not discriminate significantly between structures, we find stable low-symmetry insulating structures well into the region designated as phase III. In the atomic region, where the tendency toward low symmetry is balanced by the zero point energy which favors high coordination and symmetry, we found four-fold structures like diamond most stable [27]. At higher pressures the Madelung energy of the proton lattice will cause a transition into more close-packed structures and ultimately bcc.

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