Structure and Stability of Metallic Hydrogen

Frank E. Harris and J. Delhalle[a]
Department of Physics, University of Utah, Salt Lake City, Utah 84112
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A calculation of the electronic energy and optimum atomic spacing for an equally spaced linear array of hydrogen atoms is combined with other information to yield an improved analysis of the existence and stability of metallic hydrogen. A filamentary structure postulated by others is predicted not to be stable or metastable at any pressure; previous predictions of a transition under pressure to a metallic cubic (or hcp) phase are reaffirmed. The energies and interatom spacings in H_2, linear chains, and cubic crystals are in good accord with chemical expectations.

The last few years have seen an increasing interest in the structure and properties of metallic hydrogen. Spurred by prediction of its high-temperature superconductivity,[1,2] occurrence in Jovian planets,[3] and potential importance in laser-fusion and energy-storage applications, numerous theoretical and experimental studies have been directed at this intriguingly simple system. The experimental situation is still somewhat ambiguous, but metallic hydrogen may have been observed by Grigor'ev *et al.*[4] and by Vereschschagin, Yakovlev, and Timofeev.[5] The theoretical studies date back to an initial investigation by Wigner and Huntington[6]; a recent survey by Caron[7] summarizes the situation up to 1974.

The observability and expected properties of metallic hydrogen depend upon the crystal structure(s) in which it may form and upon the pressure range(s) in which it may be stable or metastable. The most comprehensive previous study of the probable crystal structures of metallic hydrogen is to be found in the work of Brovman, Kagan, and Kholas,[8,9] who predicted a filamentary structure to be the most favored metastable form at zero pressure, with less anisotropic structures favored at higher pressures, leading finally to a stable bcc phase at extreme compression. Brovman, Kagan, and Kholas[8,9] based their predictions on perturbation calculations carried through third order with the use of a Hubbard-type Hamiltonian.

Prediction of the conditions for absolute stability of a metallic phase has proved elusive, in large part due to difficulties in making sufficiently reliable calculations for the molecular solid. Typical results indicate the metallic phase to be stable only at pressures in or above the megabar range.[10] We have been among those studying the transition between molecular and metallic phases[11]; we find the transition to be first order, with an atomic volume change from about 17 bohr^3 (for the molecular phase) to about 11 bohr^3 (for the atomic crystal). Both phases possess atomic volumes smaller than that of the hypothetical cubic structure at zero pressure (18–19 bohr^3).

We report now a calculation for a linear array of hydrogen atoms, discussing how it, plus our earlier studies of cubic hydrogen systems,[12,13] can lead to a partial confirmation of the work of Brovman, Kagan, and Kholas[8,9] and to more reliable predictions relative to metallic hydrogen. Our calculations, to be reported elsewhere in detail,[14] give total energies, equilibrium interatomic spacing, and electronic wave functions for an infinitely long line of equally spaced hydrogen atoms. We assume doubly occupied "crystal" orbitals of "modulated-plane-wave"-type,[13] built from one 1*s* Slater-type orbital per atom, and use the usual nonrelativistic Hamiltonian (kinetic plus electrostatic energy), evaluating exactly all Coulomb and exchange matrix elements. The screening parameter of the Slater-type orbital was determined variationally. Except for the modifications inherent in the application to a system with one-dimensional periodicity,[15] the method is identical to that used in our cubic-crystal studies.

The most important result of the calculation is its prediction of an optimum interatom spacing of 1.78 bohr with an associated total energy of -0.527 hartree/atom. The wave function yielding this result had Slater screening parameter 1.217 (close to a typical value for hydrogen in molecules) and produced a ratio of potential energy to kinetic energy in good accord with the virial theorem (-2.003). The calculated energy and interatom spacing are in reasonable agreement with those previously obtained by Liskow *et al.*[16] and by Kertesz, Koller, and Azman[17]. The new feature of our results is their direct comparability with extant cubic-crystal calculations.

In earlier calculations,[12,13] we used the same orbital form and Hamiltonian on bcc and fcc structures. For the bcc crystal, we found the optimum nearest-neighbor distance to be 2.85 bohr, with an energy of -0.467 hartree/atom. For the fcc crystal, the corresponding quantities were 2.99 bohr and -0.468 hartree/atom. No studies were made of the hcp structure; we would expect a behavior quite similar to that of the fcc crystal. It is clear that the linear chain is both more closely spaced and more stable than either cubic structure. This fact suggests the construction of a three-dimensional crystal as a space-filling bundle of linear chains; in fact, Brovman, Kagan, and Kholas[8,9] find this to be the most stable structure at zero pressure, and to be metastable.

In order to investigate more completely such bundles of chains, we estimated the interaction energy of a pair of adjacent chains by summing the pairwise contributions of the individual hydrogen atoms, using the calculations of Kolos and Wolniewicz[18] on the interaction of nonbonded hydrogen atoms. This approach ignores three-body effects and any possible partial bond formation, but is probably adequate so long as the interchain spacing is large compared to normal bond lengths. Interaction energies obtained in this way, listed in Table I, were used as a basis for the further analysis to be presented here.

Using the information in Table I, we conclude that the most stable chain bundle will be hexagonal in cross section, each chain having six nearest neighbors. The equilibrium configuration is characterized by an interchain separation of about 7.4 bohr and a total interchain energy contribution of $-0.000\,44$ hartree/atom. This appears to be the lowest-energy potentially possible zero-pressure configuration of an atomic-hydrogen solid. The chain bundle has an atomic volume of 84 bohr^3, far smaller than that of solid molecular hydrogen (120 bohr^3). To 10^{-7} hartree/atom, this result is independent of the relative positioning of the atoms of adjacent chains, thereby confirming the assertion of Brovman, Kagan, and Kholas[8,9] that the chains should be able to slip freely relative to each other.

TABLE I. Calculated interaction energy E (hartree/atom) for two chains of hydrogen atoms at interchain spacing δ (bohr). The intrachain spacing is 1.78 bohr; to the precision given E is independent of the relative longitudinal positioning of the two chains.

δ	E	δ	E
3.4	0.0361	6.9	$-0.000\,117$
3.5	0.0314	7.0	$-0.000\,127$
3.6	0.0274	7.3	$-0.000\,143$
3.8	0.0206	7.4	$-0.000\,144$
4.4	0.0083	7.5	$-0.000\,143$
5.0	0.0031	7.6	$-0.000\,142$

However, we disagree with Brovman, Kagan, and Kholas[8,9] as to the metastability of the filamentary structure at zero pressure. The calculations of Kertesz, Koller, and Azman[17] on chains of unequally spaced hydrogen atoms show that the equally spaced chain will be unstable relative to the expansion of alternate spacings, permitting the chain to explode along its linear dimension into separated hydrogen molecules. The slight attraction between chains is insufficient to counteract this destabilizing effect.

We next consider the optimum configuration of the atomic crystal when under compression. Continuing our analysis of the filamentary structure, we note that the minimum pressure at which there is any chance of metastability will be that which just suffices to prevent the "explosion" referred to in the preceding paragraph. Using values (from Ref. 17) of the change in linear-chain energy with respect to expansion toward H_2 molecules, we can estimate the longitudinal force which must be applied to each chain. Then, using Table I, we can allow for the effect of pressure on the interchain separation and invoke the requirement of hydrodynamic stability. Such a calculation indicates a minimum pressure of 0.71 Mbar, with the interchain spacing reduced to about 4.55 bohr (equivalent to an atomic volume of 32 bohr^3), and with total interchain repulsion energy of about $+0.020$ hartree/atom. At this density the interaction between adjacent chains is still independent of their relative longitudinal positioning to 10^{-5} hartree/atom.

In addition to possessing hydrodynamic stability, we calculate the compressed structure discussed in the preceding paragraph to be stable with respect to the rearrangement of each linear chain into H_2 molecules. We are nevertheless pessimistic as to metastability because of the multifold possibilities for few-atom rearrangements into a favored structure of the molecular crystal. Nowhere in the relevant atomic-volume range of the filamentary structure (32–22 bohr^3) is it even close in energy to the molecular crystal.[11]

Referring once again to Table I, we may estimate the change in energy of the filamentary structure as it is compressed into volumes smaller than that at which it initially becomes hydrodynamically stable. When the interchain separation has been reduced to about 3.80 bohr (atomic volume 22.3 bohr^3), the total energy has risen to become equal to that of the fcc structure (-0.465 hartree/atom). Below this atomic volume, the cubic structures are energetically favored over the filamentary structure. Since the transition from molecular to atomic crystal has been calculated to take place at smaller volumes than are in question here, the analysis in terms of a cubic atomic crystal would appear to remain appropriate.

There remains one possibility discussed by Brovman, Kagan, and Kholas,[8,9] namely the formation of planar sheets of hydrogen atoms which could stack to form arrays of lower than cubic symmetry. A complete discussion of this possibility would entail a good quantum-mechanical calculation for a sheet of atoms, and we have not as yet performed such a study. However, a sheet structure would have no effect on the present analysis unless there were a volume range in which it was more stable than both the cubic and molecular phases. On the basis of the information available now, this eventually does not appear very likely.

Both the linear-chain calculations and the present analysis are consistent with reasonable chemical expectations regarding an atomic-hydrogen lattice. The nonexistence of valence-shell p orbitals effectively limits hydrogen to one strong bond (as in H_2, with a bond length of 1.4 bohr); all additional neighbors have a net antibonding interaction. The unusually large optimum near-neighbor distances in the cubic crystals (2.85–2.99 bohr) represent an optimum "partial bonding" of each atom to several neighbors; that in the linear chain (1.78 bohr) represents a "half-bonding" situation.

In summary, we conclude that a metastable filamentary structure for metallic hydrogen is unlikely to be realizable, and that the most reasonable expectation is for the production of a stable cubic or hcp structure at high pressure.

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[a] Permanent address: Laboratoire de Chimie Théorique Appliquée, Facultés Universitaires Notre-Dame de la Paix, Rue de Bruxelles 61, B-5000 Namur, Belgium.

[1] N. W. Ashcroft, Phys. Rev. Lett. 21, 1748 (1968).

[2] T. Schneider and E. Stoll, Physica (Utrecht) 55, 702 (1971).

[3] W. B. Hubbard and R. Smoluchowski, Space Sci. Rev. 14, 599 (1973).

[4] F. V. Grigor'ev, S. B. Kormer, O. L. Mikhailova, A. P. Tolochko, and V. D. Urlin, Pis'ma Zh. Eksp. Teor. Fiz. 16, 142 (1972) [JETP Lett. 16, 201 (1972)].

[5] L. F. Vereschchagin, E. N. Yakovlev, and Yu. A. Timofeev, Pis'ma Zh. Eksp. Teor. Fiz. 21, 190 (1975) [JETP Lett. 21, 85 (1975)].

[6] E. Wigner and H. B. Huntington, J. Chem. Phys. 3, 764 (1935).

[7] L. G. Caron, Comments Solid State Phys. 6, 103 (1975).

[8] E. G. Brovman, Yu. Kagan, and A. Kholas, Zh. Eksp. Teor. Fiz. 61, 2429 (1971) [Sov. Phys. JETP 34, 1300 (1972)].

[9] E. G. Brovman, Yu. Kagan, and A. Kholas, Zh. Eksp. Teor. Fiz. 62, 1492 (1972) [Sov. Phys. JETP 35, 783 (1972)].

[10] See, for example, E. Østgaard, Phys. Lett. 45A, 371 (1973).

[11] D. E. Ramaker, L. Kumar, and F. E. Harris, Phys. Rev. Lett. 34, 812 (1975).

[12] F. E. Harris, L. Kumar, and H. J. Monkhorst, Int. J. Quantum Chem. 5S, 527 (1971).

[13] F. E. Harris, L. Kumar, and H. J. Monkhorst, Phys. Rev. B 7, 2850 (1973).

[14] J. Delhalle and F. E. Harris, to be published.

[15] F. E. Harris, J. Chem. Phys. 56, 4422 (1972).

[16] D. H. Liskow, J. M. McKelvey, C. F. Bender, and H. F. Schaefer, Phys. Rev. Lett. 32, 933, 1331(E) (1974).

[17] M. Kertesz, J. Koller, and A. Azman, Theoret. Chim. Acta 41, 89 (1976).

[18] W. Kolos and L. Wolniewicz, J. Chem. Phys. 43, 2429 (1965).