Reprinted from:
1972, *Phys. Earth Planet. Interiors* 6, 60–64. North-Holland Publishing Company, Amsterdam
Printed in the Netherlands

53
43

CORRELATION OF THEORY AND EXPERIMENT FOR HIGH-PRESSURE HYDROGEN*

WILLIAM G. HOOVER, MARVIN ROSS, C. F. BENDER, FORREST J. ROGERS and R. J. OLNESS

Lawrence Livermore Laboratory, University of California, Livermore, Calif. 94550, U.S.A.

Recent quantum calculations and high-pressure experiments both agree on the magnitude of the forces with which hydrogen molecules interact. The calculated forces have to be determined in two steps: the repulsion is determined by Hartree–Fock calculations while the attraction is deduced semiempirically. The "experimental" forces are inferred from recent data on hydrogen shock-compressed to 214 kbar. The agreement indicates the usefulness of a pair-potential description of dense hydrogen and suggests, using potentials consistent with both theory and experiment, that pressures of at least 1.7 Mbar will be required to make metallic hydrogen. The expected lifetime of the metal at atmospheric pressure is very short.

1. Introduction

Hydrogen is of interest because it is simultaneously the simplest, commonest, and most dangerous of the elements. Hydrogen appears simple because it has only two electrons per molecule. Despite this apparent simplicity, convincing calculations of its thermodynamic properties have not been carried out. This is because the forces with which hydrogen molecules interact are not yet understood in a fundamental way. Despite its overwhelming abundance in the solar system, most of that hydrogen exists under esoteric thermodynamic conditions hard to duplicate in terrestrial laboratories. In the Sun, fusion maintains temperatures of several million degrees. Pressures in Jupiter and Saturn are near 100 Mbar so that the hydrogen in the centers of these planets is compressed to less than 1% of the normal liquid volume (DeMarcus, 1958). Despite its ultimate importance as a source of fusion power, practical application of the source still appears to lie decades in the future.

Recently, both the theoretical and the experimental studies of this fundamental material have become more sophisticated. The theoretical calculations of the H_2–H_2 interaction appear at last to be converging with inferences made from high-pressure experiments. The new experiments, carried out by Van Thiel and Hord at Livermore (Van Thiel, 1972) and by Dick at Los Alamos (Kerley, 1971) have pushed direct experimental knowledge of the equation of state of hydrogen to a pressure of 214 kbar and a temperature of order 5000 K. In view of these new theoretical and experimental advances, it is the appropriate moment to look at the extent of the agreement between them and to see what conclusions can be drawn from the comparison and applied to further advances in the study of hydrogen.

The most interesting form of hydrogen has not yet been directly observed on Earth, although it is supposed to be the principal component of both Jupiter and Saturn. This is metallic hydrogen. In addition to possible applications as a room-temperature superconductor or fusion fuel (Ashcroft, 1968), there is intrinsic interest in metallic hydrogen as the simplest alkali metal. Because the metal would be metastable at atmospheric pressure, or at any other pressure less than that required to produce it, the initial production is technologically complicated. The tremendous compressions required (nearly tenfold from the normal liquid volume) rule out direct shock experiments. Instead, as described here by Ron Hawke, isentropic compression with high magnetic fields, or huge static presses (Gross, 1970) should eventually lead us to an experimental, rather than just theoretical, description of the metal.

---

* This work was performed under the auspices of the United States Atomic Energy Commission.

2. What are the forces in hydrogen?

2.1. *Theoretical*

Theoretical descriptions of the H_2–H_2 interaction are still incomplete. In principle, we would like to use the Schrödinger equation to determine the energy of the ground state of four electrons in the presence of four protons with two of the proton–proton distances fixed in the vicinity of the experimental H–H distance in hydrogen, namely 1.4 bohr* (about 0.75 Å). In order to calculate accurate low-pressure thermodynamic properties, we would need to know this energy accurately. A tolerable uncertainty would be 10^{-5} hartree**, corresponding to $\frac{1}{10}$ the attractive interaction between two molecules. In practice, the best calculations so far carried out (Tapia *et al.*, 1971; Bender and Schaefer, 1972) are too high in total energy by about 10^{-2} hartree. Until better functional forms for molecular wavefunctions are developed to improve this situation, we will have to continue to rely on approximate calculations of the H_2–H_2 interaction in which the energy relative to separated molecules is used rather than the absolute energy with its unacceptably large errors.

The results of Schaefer *et al.* (1970) for the simpler four-electron problem of two interacting helium atoms indicate that the interaction problem can be separated into repulsive and attractive parts. We will use the same separation in describing the H_2–H_2 interaction. The repulsive forces can be approximated by a Hartree–Fock calculation in which two molecules are allowed to interact without any explicit correlation between the electrons in one molecule and those in the other molecule. The Hartree–Fock wavefunction does not account for the long-range attractions (dispersion forces) arising from explicit electron correlation. The helium results indicate that the dispersion energy terms of order R^{-6} and R^{-8} closely approximate the difference between the Hartree–Fock repulsive energy and the total interaction energy.

An extensive series of computer studies of the H_2–H_2 interaction was carried out by Magnasco and his coworkers (Magnasco *et al.*, 1967). These authors used single 1s exponential orbitals as bases for molecular orbitals. The resulting interaction energies depended strongly on the angular orientations of the two interacting hydrogen molecules; the ratio of the energy for the colinear parallel configuration $\circ\!-\!\circ\ \ \circ\!-\!\circ$ was approximately five times that of the rectangular parallel configuration obtained by rotating each molecule 90° in the plane of the paper. Unfortunately, the thermodynamic properties obtained from the Magnasco repulsion (Neece *et al.*, 1971) disagreed with experimental data. Predicted pressures at 0 K were about a factor of two above the experimental data. The discrepancy could be explained either by experimental error or by theoretical inadequacy of the wavefunctions. More extensive calculations of the H_2–H_2 repulsion were carried out (Tapia *et al.*, 1971; Bender and Schaefer, 1972) combining both spherical (s-type) and angle-dependent (p-type) Gaussian functions on each proton to build up molecular orbitals. The results were a substantially reduced repulsion with a much smaller angle dependence, only a factor of two variation between the highest and lowest energies at fixed intermolecular separation R. The reduced angular variation from these new results is small enough so that zero-point energy provides relatively free rotation over the whole range of densities for which the solid phase is stable. A spherical average over the four orientations for which the quantum Hartree–Fock calculations have been carried out gives the repulsive part of the H_2–H_2 interaction:

$$\begin{aligned}\phi_{\text{repulsion}} &= \tfrac{1}{9}\left[2 \begin{smallmatrix}\circ\\ |\\ \circ\end{smallmatrix}\ \begin{smallmatrix}\circ\\ |\\ \circ\end{smallmatrix} + 2 \begin{smallmatrix}\circ\\ |\\ \circ\end{smallmatrix}\ \circ + 4 \begin{smallmatrix}\circ\\ |\\ \circ\end{smallmatrix}\ \circ\!-\!\circ + \circ\!-\!\circ\ \circ\!-\!\circ\right]_{\text{HF}}\\ &= 8.2\exp[-1.74R],\end{aligned}$$

in hartrees, where R, the center-to-center H_2–H_2 separation, is measured in bohrs. It is interesting to note that over the range from 3 to 8 bohr this potential agrees with that derived by Trubitsyn (1966), 12.15 exp $(-1.81R)$, within 20%. Trubitsyn's calculation was based on averaging the interactions of hydrogen *atoms* over spherical surfaces. The spheres were centered at distance R apart, and the sphere radii were half the experimental H–H separation. The new theoretical repulsive potential is shown in fig. 1. The corresponding spherical average of the older Magnasco repulsion is also shown; the difference between the two is approximately a factor of 2.

The attractive part of the H_2–H_2 interaction has been determined by a combination of experimental and theo-

---

* 1 bohr = 1 atomic unit of length = a_0.

** 1 hartree = 1 atomic unit of energy = e^2/a_0.

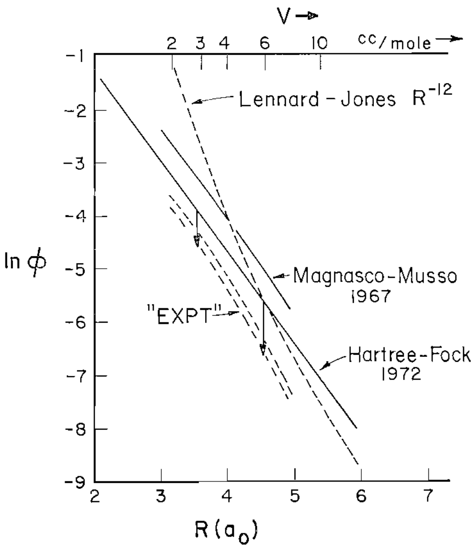

Fig. 1. Pair potentials for the H_2–H_2 interaction. The potential (in hartrees) is plotted on a logarithmic scale as a function of R (in bohrs), the distance between molecular centers. The volume scale at the top of the figure indicates the volume occupied by a mole of H_2 in a close-packed structure with nearest-neighbor distance equal to R. The two theoretical calculations of the repulsive interaction are shown as solid lines; the repulsive part of the low-density Lennard–Jones potential is also shown. The arrows indicate the shift in potential corresponding to the attractive dispersion energy. When the best theoretical repulsion and the semiempirical attraction are combined, the result (bottom of the arrows) is in agreement with the pair potential deduced from the shock experiments.

retical efforts. The large-R expansion has been derived from experimental oscillator strengths (DALGARNO, 1967):

$$\phi_{\text{attraction}} = -13R^{-6} - 116R^{-8}.$$

This attractive potential agrees fairly well with empirical potentials fitted to gas-phase virial and transport coefficients. The total interaction energy obtained by combining the repulsive and attractive parts is also shown in fig. 1 by arrows. At high density, the attraction can be expected to be damped. Trubitsyn suggested, using the observed H–H damping, a multiplicative factor of $\exp(-400R^{-6})$, for the H_2–H_2 attraction too. This cuts the attractive part of the energy in half at about $R = 3$ bohr, corresponding to a molar volume of about 2 cm^3/mole H_2.

2.2. *Experimental*

Until Van Thiel and Alder (VAN THIEL and ALDER, 1966) determined the density of hydrogen shock-compressed from the normal liquid volume to a pressure of 40 kbar, there were no data beyond the 20 kbar maximum reached by STEWART (1956) in static experiments. Two techniques using explosives to generate high pressures have extended the experimental results to much higher pressures. Ron Hawke has described here his magnetic implosion experiments, which correspond to isentropic compression, and Norris Keeler has described recent Livermore shock experiments along the Hugoniot pressure–volume curve which links low-pressure liquid hydrogen with high-pressure high-temperature states through a rapid adiabatic shock process. The shock experiments provide higher temperatures than do the isentropic compressions because more of the compression energy is converted into thermal motion. The combination of high temperature and pressure is particularly valuable for exploring intermolecular forces at small separations. This unique characteristic of the shock experiments makes them particularly useful for extrapolation to even higher pressures. For example, in the highest-pressure shock experiments, the temperature is about 5000 K and the molar volume about 7 cm^3. The collision diameter from the repulsive H_2–H_2 potential is about 3.6 bohr under these conditions, which corresponds to the nearest-neighbor separation in a crystal compressed to about 3 cm^3, near the volume at which hydrogen becomes metallic. Thus the shock experiment tests the potential function over a wider range of distances than can conventional static experiments.

In fig. 2, we show the pressure–volume states reached in the Livermore experiments together with Dick's Los Alamos experiments as reported by KERLEY (1971). Although some of the experiments used hydrogen and others deuterium, under slightly different initial conditions, we have adjusted the data shown in fig. 2 to compensate for these minor differences. Thus all the data shown correspond to deuterium compressed from an initial liquid volume of 23.8 cm^3/mole. Despite the scatter in the experimental data one can, for a given form of the H_2–H_2 potential function, determine bounds on the parameters in the potential. For example, two exponential-6 potentials provide reasonable upper and lower bounds on the effective potential consistent with the shock experiments. The two Hugoniot curves drawn in in fig. 2 correspond to the pair potentials $7.8e^{-1.71R} - 17R^{-6}$ and $11.7e^{-1.79R} - 16R^{-6}$. The two

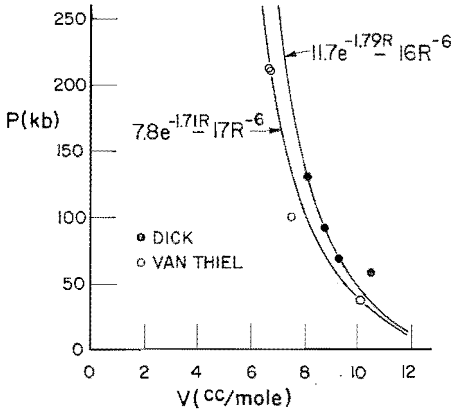

Fig. 2. Experimental determination of the H_2–H_2 interaction from shock experiments. The pressure–volume results of Van Thiel and Dick are plotted on a common scale, taking into account the slight differences among the various initial conditions of the experiments. The various experimental data on H_2 and D_2 are consistent with the range of effective pair potentials of the exponential 6 form lying between the two solid curves.

potentials are shown also in fig. 1 for comparison with the theoretical potential obtained by adding $\phi_{\text{repulsion}}$ from the Hartree–Fock calculations to $\phi_{\text{attraction}}$ from the measured oscillator strengths. We see that the theoretical and experimental results for the H_2–H_2 interaction are consistent with one another. This new result is of fundamental importance. Besides indicating that dense molecular hydrogen can be described with a pairwise-additive potential function, the agreement using the newer quantum calculations resolves the factor-of-two discrepancy between the less accurate calculations based on Magnasco's potential and experiment.

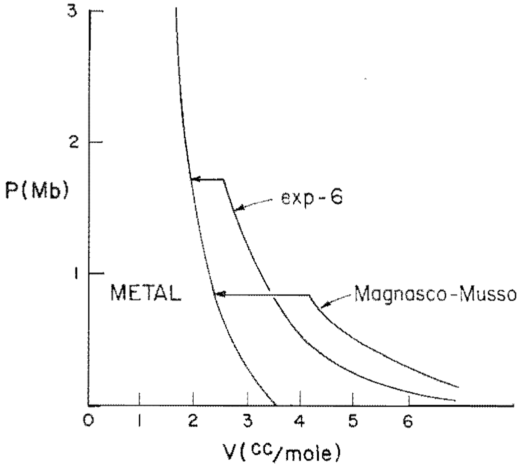

Fig. 3. 0 K isotherm for hydrogen showing the transition from the low-pressure molecular solid to the high-pressure metallic form. The lower transition, at 840 kbar, is based on the obsolete theoretical calculations of MAGNASCO *et al.* (1967). The upper curve, with a transition pressure of 1.7 Mbar, is based on the steeper of the two potentials shown in fig. 2. The upper curve establishes a lower limit for the transition pressure consistent with the Hugoniot shock experiments.

3. Metallic hydrogen

WIGNER and HUNTINGTON (1935) attribute to Bernal the observation that any material becomes metallic at high pressures. Since the energies required to free valence electrons are a few electronvolts, the pressures required are of the order of megabars (1 eV corresponds with 1 Mbar · cm^3).

For hydrogen, the properties of the metallic phase are more easily calculated than are those of the heavier alkali metals. This is because the core potential for hydrogen is the pure Coulomb potential. The major complications in the metallic hydrogen calculations lie in the nonuniformity of the electronic density (varying by a factor of six from a nuclear to an interstitial position) and in the importance of the zero-point energy (which makes a contribution equal to about $\frac{1}{4}$ of the crystal's binding energy relative to isolated atoms). Rogers has carried out a self-consistent field calculation of the properties of metallic hydrogen using local exchange and correlation potentials and including the effect of zero-point motion (NEECE *et al.*, 1971). He approximated the necessary integrals over Wigner–Seitz polyhedra by integrating over spheres instead. More recent Hartree–Fock calculations of the electronic structure of metallic hydrogen (HARRIS *et al.*, 1971) have shown that the Fermi surface for metallic hydrogen is indeed nearly spherical, just as in an ideal electron gas, so that Rogers' approximate integrations should be quite close to the truth.

As a check on his metallic calculations, Rogers carried out parallel calculations for lithium and sodium, comparing his theoretical results with experimental compressibility data (which extend to about 200 kbar) and obtaining excellent agreement in both cases. This impressive correspondence with experiment suggests that his metallic hydrogen calculations are the best now available. The theoretical zero-pressure volume of the metallic phase is 3.5 cm^3/mole H_2 corresponding to eight-fold compression from the normal liquid state. It is not yet known if it will prove possible to observe the metastable portion of the metallic hydrogen isotherm at lower pressures than that required to make the metal. Although the metal is stable relative to isolated hydrogen atoms by 0.059 hartree/molecule H_2, the molecular phase is more stable than the isolated atoms by 0.16 hartree/molecule H_2. Thus if the cold metal were to decompose to the molecular form, the energy given off, about 3 eV per molecule formed, would leave the molecular phase at a temperature of several 1000 K.

Considering that the metal has never been directly observed, it seems paradoxical that its thermodynamic properties are better understood at high pressure than are those of the solid molecular phase. But knowledge of molecular-phase properties is crucial in determining whether or not a proposed experiment will reach conditions at which the metal is more stable. How much pressure is required to stabilize the metallic form relative to the molecular form? The most straightforward predictions are based on the shock experiments. Two pair potentials shown in fig. 1 are consistent with the shock data; the more repulsive one predicts that, if the hydrogen were kept cold, the transition from the molecular solid to the metallic one would occur at 1.7 Mbar – this is to be contrasted with the earlier prediction of 0.84 Mbar based on the purely theoretical calculations of Magnasco *et al.* If the softer potential consistent with the shock data were used, it would be difficult to pin down the transition pressure, principally because the form of the attraction at high density is uncertain. Presumably, the molecular phase would be rather similar to the description of TRUBITSYN (1966) or LIBERMAN (1971), leading to transition pressures between 2 and 3 Mbar.

At present, the experimental data are not accurate enough to furnish a clearcut prediction of the transition density and pressure. Additional shock experiments will clear up the uncertainty. The experiments planned in the range of a few Mbar should also serve to furnish experimental, rather than just theoretical, metallic-phase properties soon.

The possibility that metastable metallic hydrogen could be preserved at low pressure has been suggested by Ashcroft. CHAPLINE (1972) considered the instability of metallic atoms to recombination within the crystal and obtained lifetimes less than 1/s for the zero-pressure metal, SALPETER (1972) has just carried out a semiclassical tunneling calculation which indicates that even with optimistic assumptions a crystal of metallic hydrogen could persist at low pressure for no more than 100 s. About the same kinds of estimates can be obtained by considering the probability that particles will link up to form molecules on the crystal surface due to zero-point vibration. In any event, despite the technological importance of a room-temperature superconductor, it appears that metallic conductivities for hydrogen will always be measured at high pressure. Such high pressure experiments are still of great intrinsic interest for the light they will shed on fundamental quantum-mechanical calculations and the structure of the solar system.

References

ASHCROFT, N. W. (1968), Phys. Rev. Letters **21**, 1748.

BENDER, C. F. and H. F. SCHAEFER (1972), Private communication.

CHAPLINE, G. F. (1972), Phys. Rev. **6B**, 2067.

DEMARCUS, W. C. (1958), Astron. J. **63**, 2.

DALGARNO, A. (1967), Adv. Chem. Phys. **12**, 143.

GROSS, E. (1970), Science News **97**, 623.

HARRIS, F. E., L. KUMAR and H. J. MONKHORST (1971), Intern. J. Quantum Chem. Symp. **5**, 527.

KERLEY, G. I. (1971), *A new model of fluids*, Los Alamos Sci. Lab. Rept. LA-4760, Los Alamos, New Mexico.

LIBERMAN, D. A. (1971), *Equation of state of molecular hydrogen at high pressure*, Los Alamos Sci. Lab. Rept. LA-4727-MS, Los Alamos, New Mexico.

MAGNASCO, V., G. F. MUSSO and R. MCWEENY (1967), J. Chem. Phys. **46**, 4015; ibid. **47**, 1723, 4617, 4629.

NEECE, G. A., F. J. ROGERS and W. G. HOOVER (1971), J. Computational Phys. **7**, 621.

SALPETER, E. E. (1972), Phys. Rev. Letters **28**, 560.

SCHAEFER, H. F., D. R. MCLAUGHLIN, F. E. HARRIS and B. J. ALDER (1970), Phys. Rev. Letters **25**, 988.

STEWART, J. W. (1956), J. Phys. Chem. Solids **1**, 146.

TAPIA, O., G. BESSIS and S. BRATOŽ (1971), Intern. J. Quantum Chem. Symp. **4**, 289.

TRUBITSYN, V. P. (1966), Soviet Phys.-Solid State **7**, 2708.

VAN THIEL, M., M. ROSS, W. G. HOOVER, B. L. HORD, W. H. GUST, A. MITCHELL, M. D'ADDARIO, R. N. KEELER, W. M. ISBELL and K. BOUTWELL (1972), Bull. Am. Phys. Soc. **17**, 659.

VAN THIEL, M. and B. J. ALDER (1966), Molecular Phys. **10**, 427.

WIGNER, E. and H. B. HUNTINGTON (1935), J. Chem. Phys. **3**, 764.