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Wigner and Huntington: the long quest for metallic hydrogen

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In 1935, Wigner and Huntington (WH) predicted that at a density $D_{Met} = 0.62$ mole H/cm^3, 'very low temperatures', and a pressure greater than 25 GPa, body-centered cubic H$_2$ would undergo an isostructural phase transition directly to H with an associated insulator-metal transition (IMT). WH also predicted an H$_2$ structure type that might occur if the simple H$_2$/H dissociative IMT does not exist: 'It is possible … that a layer-like lattice … is obtainable under high pressure'. In 1991, Ashcroft predicted that the 'geometric and dynamic nature of the (H–H) pairing', possibly in a layered graphite-like structure, would substantially impede achieving metallic H$_2$. In 1996, metallic fluid H was made under dynamic compression at 0.64 mole H/cm^3, 140 GPa and $T/T_F \ll 1$, where T_F is Fermi temperature. In 2012, a layer-like lattice, called Phase IV, was discovered above ~220 GPa static pressure. Phase IV is insulating and possibly semi-metallic up to ~360 GPa, above which it has been predicted to become metallic. This paper is a historical perspective – a comparison of WH's predictions with recent dynamic, static and theoretical high pressure results. WH did extremely well.

Keywords: H metallization; dynamic compression; static compression; high pressures

PACS: 62.50.-p; 72.15.Cz; 71.30.+h; 33.15.Fm

1. Introduction

Metallization of hydrogen has been a major experimental quest in Condensed Matter Physics and Chemistry ever since Wigner and Huntington (WH) predicted that at a density $D = 0.62$ mole H/cm^3 ($r_s = 1.63$), 'very low temperatures', and a pressure P much greater than 25 GPa, electrically-insulating solid bcc (body-centered cubic) H$_2$ would undergo a sharp isostructural dissociative phase transition directly to solid H with an associated insulator-metal transition (IMT) [1]. WH's calculational model, predates development of electron band theory, the invention of the electronic computer, and the development of modern ultrahigh pressure experimental techniques. The purpose of this paper is to compare WH's predictions with recent experimental results under dynamic and static compression and recent theory. WH did extremely well.

WH's 2-component dissociation/metal model is relatively simple because computational technology then consisted of pencil, paper, and mechanical adding machine. WH calculated total energies of bcc H$_2$ and H versus lattice parameter by summing individual contributions, including zero-point energies, in analytic forms. WH probably chose the bcc structure because at sufficiently high pressures, protons in a lattice of H atoms interact via an unscreened Coulomb potential and the crystal structure that minimizes Coulomb potential energy is bcc.

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Their calculated density of that IMT, $D_{Met} = 0.62 \, \text{mol H/cm}^3$, is the density on increasing pressure at which total energy of H becomes less than total energy of H_2. Because this calculated density is so large, 7.4-fold of solid-H_2 density, solid H at D_{Met} was expected to be a metal and thus dissociation would be accompanied by an IMT. This expectation is borne out by modern theory. A bcc lattice of monatomic H is predicted theoretically to metallize at $r_s = 2.3$–2.2 [2,3], which corresponds to a substantially lower H density than WH's $r_s = 1.63$, and thus is justification for considering fluid H dissociated from H_2 to be metallic.

Because D_{Met} is so large, the corresponding metallization pressure was well beyond high pressure technology of those days. Thus, a careful calculation of P_{Met} could not have motivated an experimental test of their theoretical prediction. So, WH simply calculated a lower bound on metallization pressure, 25 GPa, by assuming H_2 compressibility is constant with increasing pressure, rather than decreasing, the usual case.

Metallization of H has been obtained by dynamic compression, which is fast and dissipative. Thus, those (P, D, T) conditions were achieved on completion of a cross over rather than at a sharp isostructural transition. The difference between D_{Met} predicted theoretically by WH and measured D_{exp} is 3%, well within uncertainties of both methods. Relative to initial liquid-H_2 or solid-H_2 densities of 0.071 or 0.086 g/cm^3, respectively, compression at D_{exp} is 9.0-fold or 7.4-fold, respectively. The likely reason why fluid H_2 at 3000 K becomes metallic H at 140 GPa and why solid H_2 at 300 K and ~360 GPa does not is discussed in Section 4.

2. Dynamic compression

Metallic fluid hydrogen has been made under dynamic compression at density $D_{exp} = 0.64 \, \text{mol H/cm}^3$ ($r_s = 1.62$), $P = 140$ GPa and temperature $T \sim 2600$ K [4–6]. Those states were obtained by multiple-shock compression generated by a shock wave reverberating in liquid H_2 initially at 20 K contained between two sapphire (single-crystal Al_2O_3) anvils. Samples were 25 mm in diameter and 0.5 mm thick. A multiple-shock pulse was induced by impact onto a cryogenic sample holder by either an Al or Cu plate accelerated to a velocity in the range 5.6–7.3 km/s with a two-stage light-gas gun. Pressures generated by those impacts were in the range 90–180 GPa.

Conductivity voltage to obtain electrical conductivity σ in each of those 10 experiments was measured during the 100 ns in which dynamic pressure reverberated up to the peak pressure and then for another 50 ns in which fluid hydrogen sat quiescent in thermal equilibrium. Reported (P, D, T, σ) values correspond to the ~50-ns quiescent period in each experiment. Experimental lifetimes were ~100 ns, too brief for hydrogen to diffuse out of its holder and sufficiently long to thermally equilibrate to a temperature. Electrical conductivity increases almost four orders of magnitude from 90 GPa, 0.58 mol H/cm^3 and 2100 K up to 140 GPa, 0.64 mol/cm^3 and 2600 K. Electrical conductivity is then constant at 2000/(Ω-cm) from 140 GPa up to 180 GPa, 0.76 mol H/cm^3 and 2900 K. Between 90 and 140 GPa fluid H is a semiconductor with conduction electrons thermally excited across an energy gap, which closes with density to $\sim k_B T$ at ~0.64 mol/cm^3; from ~0.64 mol/cm^3 at 140 GPa up to 0.76 mol H/cm^3 at 180 GPa thermal excitation is quenched and fluid H is a poor metal [5]. Final temperature in each experiment was calculated but was partially constrained by experimental data, as discussed below.

Measured electrical conductivity of 2000/(Ω-cm) is typical of liquid metals and highly disordered alloys. If conduction electrons are scattered with a mean-free path $\lambda \sim a$, where a is average interatomic distance, then electron scattering is said to be strong. In this case, T-dependent phonon scattering is negligible, even at low temperatures, and electrical conductivity is relatively small and commonly called minimum metallic conductivity (MMC) σ_{MMC}. Measured conductivity of 2000/(Ω-cm) is in good agreement with theoretical calculations [7–9].

Energy bands of crystalline H_2 have free-electron character above 5- to 6-fold solid-H_2 density [10]. For metallic fluid H in the free-electron model at 0.64 mol electrons/cm^3, Fermi energy $E_F = 19$ eV, Fermi temperature $T_F = 220,000$ K and $T/T_F = 0.012 \ll 1$. Metals in the periodic table satisfy the condition that $T/T_F \ll 1$, as Mott said metals should [11]. For examples, T/T_F of Cs, Au, and Cu at 300 K have values of 0.017, 0.005, and 0.004, respectively. $T/T_F = 0.012$ for metallic fluid H implies it is an ordinary metal with a sharp Fermi–Dirac electron distribution.

Experimental lifetimes were ∼150 ns and time resolution of the conductivity voltage was ∼ns. Thermal equilibrium is achieved by energy exchange between atoms and/or molecules via collisions. Estimated time between atomic H collisions at D_{Met} and metallization temperature T_{Met} is ∼10^{-5} ns (10^{-14} s), more than ∼10^5 times faster than diagnostic resolution time. During the ∼100 ns experimental lifetime, each H atom experienced ∼10^7 interatomic collisions. Measured conductivity voltage histories verified that conductivity voltage was constant for ∼50 ns after the first ∼100 ns needed to complete shock reverberation to peak pressure. Metallic fluid H was in thermal equilibrium in those experiments.

Temperatures and densities in hydrogen were calculated, but were partially constrained by experiment. Temperature and density on completion of multiple-shock reverberation in each experiment were obtained by first calculating with shock-impedance matching the first-shock state in liquid H_2 and then calculating the isentrope from that first-shock state up to the final pressure achieved in the Al_2O_3 anvils. The final pressure in the Al_2O_3 anvils is the final pressure in hydrogen, independent of the hydrogen equation of state. Pressure in the Al_2O_3 anvil depends only on shock impedance matching the impact velocity measured to 0.1% and the previously measured shock-compression curves of the metal impactor, Al baseplate and Al_2O_3 anvils. A similar process was used to calculate the first shock state in the liquid H_2 sample, its shock compression and shock temperature-pressure curves [12] also having been measured previously. The first shock in H_2 produces about ∼50% of the final temperature in each experiment. The first-shock temperature and density in each experiment were obtained by shock impedance matching, using the fit to measured shock temperatures [12]. The isentrope from the first-shock state in H_2 was then calculated up to the final pressure in the Al_2O_3 anvils [12,13]. Uncertainty in this final pressure is ∼1%, which again is the final pressure in the hydrogen. Uncertainties in hydrogen D and T derived in this manner are 3% and 10%, respectively. These uncertainties are on a more rational basis than the ultraconservative 30% uncertainty in T estimated in 1999 [5]. P/T conditions at which electrical conductivities were measured are indicated in the phase diagram Figure 1.

Measured [15–17] and calculated [7,18–20] melting temperature T_{Melt} of H_2 is ∼900 K at 140 GPa. Thus, dynamically compressed metallic H at ∼2600 K is in the fluid phase. Further, because $T = ∼ 2600$ K ∼ $3T_{\mathrm{Melt}}$, atomic correlations are probably absent in metallic fluid H near D_{met} and 140 GPa. However, it is possible that as T decreases in the metallic fluid down toward the melting curve, atomic H correlations might exist at those lower Ts at 100 GPa pressures.

It is also possible that as T decreases in the metallic fluid down toward the reputed plasma phase transition (PPT) or liquid–liquid phase transition (LLPT) [9,19,20,27], *if it exists*, that atomic H correlations might exist at those lower temperatures at some pressure of the PPT around 120 GPa [27] or at pressures more than 100 GPa greater than those earlier studies, depending on the theoretical model [9]. The issue about the existence of the PPT is summarized in [9] 'While almost all FP (first-principles) simulation methods agree qualitatively on the existence of a first-order LLPT (or PPT) in high pressure hydrogen [20,27], its precise location depends on the approximations employed [9]'. (Copyright 2013 by The American Physical Society.) Given that the PPT was predicted in 1943 [28], is yet to be observed experimentally, and its calculated position is strongly dependent on models employed, it is reasonable to consider the possibility that the PPT might not exist. Experimental verification of its existence is required.

The process by which H_2 undergoes the crossover to metallic H is systematically the same for fluid H, N, O, Rb, and Cs: quantum mechanical radial charge densities on adjacent atoms
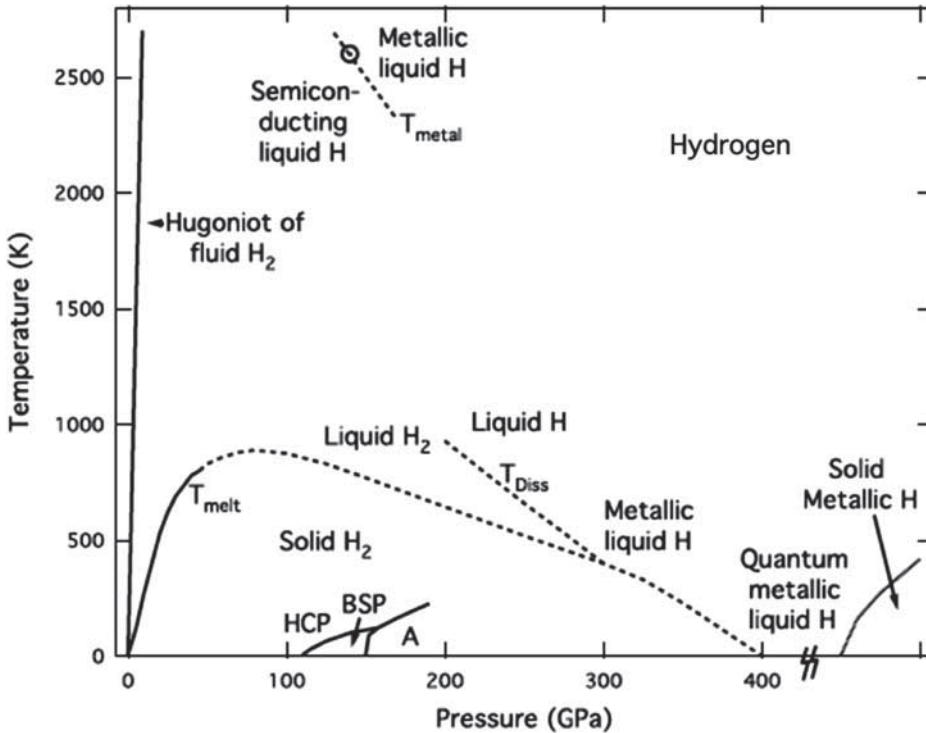
Figure 1. Approximate phase diagram of dense hydrogen [14] for illustrative purposes. Actual inclusive experimental data and theory are contained in papers in the reference list. Representative experimental work includes: (i) Open circle with dot: metallization of fluid H under multiple-shock compression at 140 GPa/2600 K determined from 10 electrical conductivity experiments [5]. Fluid hydrogen is semi-conducting from 90 GPa/2100 K up to 140 GPa/2600 K and then is a poor metal with constant conductivity of $2000/(\Omega\text{-cm})$ from 140 GPa/2600 K up to 180 GPa/2900 K. (ii) Schematic melting curve of H_2 measured [15–17] and calculated [7,18–20]. (iii) A calculated dissociation curve T_{Diss} of fluid H_2 near 250 GPa [18]. (iv) HCP, BSP, and A Phases correspond to Phases I, II, and III. The boundary between Phases III and IV (not indicated) exists at ~230 GPa at 300 K and 300 GPa at ~220 K [21]. (v) Calculated single-shock Hugoniot temperature of fluid H_2 increases linearly up to 2500 K at 4 GPa [22]. The effective pair potential used to calculate temperatures was derived by fitting measured P–V Hugoniot data of liquid D_2 and H_2 [23]. (vi) Near ground state of hydrogen is proposed to be a liquid metal [24] near 400 GPa [25], which might solidify at some higher pressure [26].

overlap and hybridize, or mix, into a metallic 1s band at sufficiently high compressions. Electrical conductivities σ have been measured at ~100 GPa dynamic pressures for H [5], N [29], and O [30] and for liquid Rb and Cs at ~2000 K at static pressures up to ~100 MPa [31]. Rb and Cs are solid metals at ambient but on heating to ~2000 K, they are semiconducting fluids. Under static pressures up to ~10^2 MPa, fluid Rb and Cs become poor metals with conductivity ~$2000/(\Omega\text{-cm})$, as fluid H, N, and O at ~10^2 GPa.

Ratios of atomic radius to average distance between atoms at which σ reaches σ_{MMC} were determined. Atomic radius is taken as effective Bohr radius a^* and interatomic distance is $D^{-1/3}$. That is, $D = 1$ atom/a^3, where a^3 is average atomic volume V_A of a cube centered on each atom in a bcc lattice. Electrical conductivities of all five elemental fluids reach σ_{MMC} at $a^*/D^{-1/3} = 0.35$ to 0.38. Rb and Cs reach σ_{MMC} but much more gradually over a substantially wider range of density than do H, N and O.

These results show that radial charge densities on adjacent atoms overlap and conduct with σ_{MMC} at sufficiently large compressions. However, the rate of increase of σ with density depends strongly on the radial extents of outermost atomic electrons, which are strongly dependent on electron screening by core electrons. These expectations are consistent with calculated radial

extents of charge density distributions of the various elements, $4\pi r^2 \psi^*(r)\psi(r)$ versus radius r, where $\psi(r)$ is the spherically symmetric wave function of the outermost s electron of H, Rb, and Cs or the spherically averaged wave function of the outermost 3p and 4p electrons of N and O, respectively, [29].

For the sake of completeness, D_{exp} is in reasonably good agreement with the pre-Quantum Mechanics Herzfeld criterion [32], which says that metallization of a system of N non-interacting atoms each with atomic polarizability α happens at density D_{mH} given by the relation $(4\pi/3)\alpha D_{mH} = 1$. For H atoms, $D_{mH} = 0.595$ mol H/cm^3 [33]. While the agreement between D_{mH} and $D_{exp} = 0.64$ mol H/cm^3 is reasonably good, it is fortuitous. Hydrogen metallization does not occur in a system of non-interacting particles. Rather, it occurs via overlap of QM radial charge-density distributions of H 1s^1 wave functions into a hybridized 1s band at high densities, as discussed in the previous paragraph.

3. Static compression and theory

WH realized there was no *a priori* reason why their classic IMT should exist. Remarkably, WH said in 1935 that 'It is possible … that a layer-like lattice … is obtainable under high pressure'. Further, 'The different layers are bound together, however, more weakly, perhaps by van der Vaals forces'. While WH's paper was virtually unread in the last six decades or so, their predictions have stood up very well, as evidenced by theoretical work done independently long after WH.

In 1991, Ashcroft [34] (Copyright Elsevier 1991) predicted that at high static pressures and densities, hydrogen would undergo a transition from semi-metallic to metallic behavior via a band-overlap transition, 'while retaining diatomic molecular order in a strongly dynamic environment'. Solid H_2 was assumed to be in a semi-metallic hcp-like phase. Using a free-electron model [10], it was found that the semi-metallic phase with a low density of electrons would have a 'free carrier type of optical response with rising reflectivity in the far infrared'. In addition, 'the geometric and dynamic nature of the (H–H) pairing are both crucial to the preservation of the insulating state up to the very substantial densities where its continued persistence has been experimentally confirmed'.

Because the layered-type hcp phase of H_2 is similar to graphite in terms of 'a very low density of ground state electronic charge', Ashcroft considered optical properties of graphite to gain insight into the nature of solid H_2 at very high pressures. Main conclusions are that (i) solid semi-metallic H_2 at high pressures would probably have a layered hcp-like crystal structure and (ii) paired-H bonds in that structure would maintain that semi-metallic phase to very high pressures, thus impeding the transition to a metallic phase at pressures higher than those of the layered phase. In other words, achieving metallic hydrogen via a band-overlap transition while retaining diatomic molecular order in a strongly fluctuating environment would be difficult, as evidenced by experiments up to 1991 [34], as well as up to this writing. Ashcroft predicted the crucial issues inhibiting achievement of solid metallic hydrogen in a diamond anvil cell, as discussed below.

At WH's predicted metallization density, 0.31 mol H_2/cm^3 (0.62 mol H/cm^3), H_2 static pressure is 73 GPa, based on the fit to measured P-V data on the 300-K isotherm [35]. At 73 GPa, the H_2 electronic band gap is ~8 eV [36]. This is a complex regime in terms of variations of molecular orientations, bond lengths, and c/a ratios; also, lower-energy structures have wider band gaps up to much higher densities [37].

Eremets and Troyan [38] initiated great interest and excitement in hydrogen metallization at unprecedented high pressures by reporting on experimental Raman spectra, a phase transition, metallization, and reflectivities observed visually. Unfortunately values of electrical resistivities derived from their measured electrical resistances and given sample dimensions are orders of

magnitude larger than for a metal and it is not certain to what extent hydrogen was the cause of those observations. Nevertheless, Eremets and Troyan did a great service to the high pressure community by revitalizing activity in dense-hydrogen research.

Under static compression near 300 K, metallization of solid H_2 has not been observed at pressures up to ~360 GPa by Zha et al. [39] nor by Howie et al. [40]. Based on measurements up to ~315 GPa, Howie et al. observed proton tunneling in dense hydrogen. They observed an electronic band gap in Phase IV of ~1.8 eV, which extrapolates to zero (metallization) at a minimum pressure of 375 GPa [21].

Theoretical calculations of Pickard et al. [41,42] have shown that the structure of solid H_2 at 250 to 295 GPa near 300 K, called Phase IV, consists of mixed structures of alternate layers of strongly bonded molecules and weakly bonded graphene-like sheets, a layered structure of the type WH predicted might occur if their classic IMT does not exist. At 220 GPa at 300 K, calculations of Liu et al. [43] found that Phase I transforms into an insulating mixture of ordered graphene-like H_2 layers with other layers of weakly coupled and disordered H_2 molecules. Above 242 GPa, the *Cmca* phase is stable and might be a semimetal. Liu and Ma [44] have performed calculations at pressures from 250 to 350 GPa and temperatures of 300 to 500 K to investigate structural effects of proton transfer discovered in Phase IV. Those authors found that H_2 molecules in graphene-like layers have short lifetimes and hydrogen vibration is strongly anharmonic. A predicted semi-metallic structure [45] might be a bridging structure between semi-metallic Phase IV and a metallic structure at still higher pressures. An H_2 phase has been predicted to be metallic at pressures above those of Phase IV [46]. H_2 has also been predicted to dissociate into a bct (body-centered tetragonal) monatomic H phase near 500 GPa ($r_s = 1.23$) [47].

Labet et al. investigated two hypothetical hydrogen structures, one of which transforms continuously from molecular states to monatomic states of the other via evolution of a single structural parameter above ~500 GPa, substantially higher than static pressures achieved experimentally to date. This process occurs in a region with a large range of H-H separations that are roughly equi-enthalpic. This situation 'is suggestive of dissociation of the H_2 units via a non-crystalline, amorphous, microscopically or soft state, or possibly even a liquid' and implies 'dynamical effects should be included in future theoretical studies [48]' (Copyright 2013 by the American Physical Society).

4.   Why is dense hydrogen so different under dynamic and static compression?

A key question is why is it that fluid H at ~3000 K and 140 GPa becomes metallic at 0.64 mol H/cm^3, essentially the density predicted by WH for their IMT at low temperatures; whereas metallization of solid H_2 near 300 K is yet to be observed experimentally at pressures up to ~360 GPa? The basic answer is that dynamic compression induces temperature and entropy in addition to compression; whereas static compression has relied virtually entirely on compressive $\int P \, dV$ work to drive dissociation.

Experiments and theory above 200 GPa near 300 K show solid, non-metallic, complex, stable, layered structures with strong intermolecular paired-H bonds that persist to highest pressures, ~360 GPa reported to date. On the 300 K isotherm at WH's predicted metallization density, pressure is 73 GPa. Densities at 360 GPa are well above WH's predicted IMT density at a static pressure of 73 GPa. The implication is that 'cold' compression at 300 K induces strong intermolecular paired-H bonds, which strengthen solid H_2, rather than weakening it to dissociation. A similar idea has been suggested independently [49].

On the other hand, at 3000 K and 140 GPa fluid hydrogen completes a cross over from non-metal to degenerate metallic H at the density of 0.64 mol H/cm^3, which is within 3% of WH's predicted density for the IMT directly from H_2 to H. Agreement between WHs prediction for low

temperatures with dynamic experiments at higher temperatures implies that strong intermolecular paired-H bonds do not exist in metallic fluid H at 3000 K. Thus, in dynamic experiments the cross over is probably from H_2 *directly* to H, as WH assumed in their model. It is those intermolecular paired-H bonds that have precluded dissociation in the solid at ~300 K at pressures reached thus far. Intermolecular interactions in fluid H_2 are probably weak and van der Vaals-like [50], and so fluid H_2 is very compressible. Thus, shock-induced temperature and entropy via molecular dissociation are sufficiently high to heat liquid hydrogen into the fluid at 100 GPa pressures and to provide sufficient thermal energy for dissociation and thus metallization of the fluid.

Agreement between WH, who ignored temperature in their calculations, and metallization density at 3000 K also implies thermal contributions to total energy are small compared with compressive contributions caused by high densities, not unreasonable given that 0.64 mol H/cm^3 is 7.4-fold compressed solid density and $k_B T \sim 0.3$ eV. Another implication is that the structure of solid H_2 has minimal effect on dissociation, as suggested by WH. Bond energy of the intramolecular H_2 dimer, 4.5 eV at initial liquid density, is expected to dominate energy of compression relative to energy variation with H_2 structure. At sufficiently high densities, monatomic H is expected to metallize no matter what its high-density structure is.

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