Stability of Metallic Hydrogen at Ambient Conditions

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Abstract. The possibility of metallic hydrogen was first mooted by Wigner and Huntington in 1935. Here it is show that the calculations from that paper are in remarkably good agreement with modern density functional theory results. The possibility that metallic hydrogen could be recovered to ambient pressure is often attributed to papers by Brovman et al., although in fact they only say it would be metastable with undetermined lifetime. Density functional theory calculations presented here show that reasonable candidate structures for metallic hydrogen are wildly unstable at ambient conditions, and molecular dynamics calculations show that the lifetime to which Brovman et al. refer is considerably less than a picosecond. It is concluded that the prospects of using recovered metallic hydrogen as rocket fuel or for electricity distribution may have been overstated.

1. Introduction

In 1926 J. D. Bernal proposed that all materials, when subjected to a high enough pressure, will become metallic. Several years later, Wigner and Huntington investigated the properties of a putative metallic modification of hydrogen. Their idea was that hydrogen would become atomic under pressure, and therefore behave like an alkali metal. The initial calculation by Wigner and Huntington (WH) involved a full potential solution to the Schroedinger equation within a radius $r_s$, augmented by a free-electron contribution. This calculation gives a density of 0.8 at ambient pressure and an energy much higher than molecular hydrogen, and so they concluded that the metallic phase could exist only at high pressure. A number of corrections for exchange, correlation, Madelung, zero-point nuclear fluctuations etc. in various approximations are considered, all of which increase the instability at ambient pressure.

The physics included in these calculations is rather similar to that still used in density functional calculations, although modern computing power enables us to calculate the wavefunctions self-consistently. The comparison between WH’s calculation and a modern DFT calculation for bcc hydrogen is shown in Figure 1, where one sees immediately that the agreement is rather good. This may be a surprise, since one commonly sees statements such as “Wigner and Huntington predicted a transition pressure of 25GPa”. In fact this 25GPa value is given as a lower bound, presented by WH to demonstrate the impossibility of making metallic hydrogen with contemporary equipment: WH also say “if the compressibility at ordinary pressures would hold throughout, the molecular form would be stable for all volumes” (i.e. the transition pressure is infinite). WH presciently mention layered structures, but their considered transition goes directly from a molecular insulator to atomic free-electron material, and in the most recent report of metallic hydrogen, Dias and Silvera show a reflectivity corresponding to such a free electron metal. However most DFT calculations suggest that metallisation may first occur via band-gap closure in a molecular solid, with the atomic solid appearing at higher pressures.

The exciting properties claimed for metallic hydrogen, such as room temperature superconductivity, are expected in the atomic phase, so it is the recovery of this phase which...
we consider. The idea of recoverability of atomic hydrogen is typically associated with the 1974 work of Brovman et al\[4\]. They apply a model similar to WH, with a perturbative approach and simplifying assumptions, e.g. “the correlation energy has practically no influence on the determination of the optimal structure”. They test a number of possible crystal structures and find that the Wigner-Huntington-type monoatomic structures tend to be unstable with respect to unit cell doubling (a precursor to molecule formation). Like WH, they find that the metallic phases have an energy minimum corresponding to zero pressure and state that there should be a “phase locally stable in all the macroscopic parameters”, which is stable relative to atomisation but has higher energy than the molecular phases. Unfortunately, many readers have failed to notice that the caveat “macroscopic parameters” involves only a limited range of possible instabilities. They consider only affine deformations (i.e. elastic instabilities), and not phonons. This has led to a misapprehension that Brovman’s work predicts a recoverable metallic state, ignoring Brovman’s subsequent statement that the lifetime of this state “remains open”.

Perhaps the most curious aspect of this is why Brovman’s work is still regarded as plausible when lattice dynamics calculations which probe both microscopic and macroscopic deformations have been routine for many years. Self-consistent methods of calculating electronic structure, in particular DFT, are able to treat both metallic and covalent bonding within the same microscopic theory. Chemically, one would expect the instability of atomic hydrogen to be towards formation of molecules, however the tests of stability against affine deformations carried out by Brovman do not allow such pairing in dense hydrogen.

The question of finding the most stable arrangement of atoms has been tackled in the seminal paper by Pickard and Needs\[6\], and subsequently by a number of other authors\[7, 8\]. From this work, the most likely candidate structure for atomic metallic hydrogen has emerged as the four-fold coordinated \(I4amd\).

2. Calculation Details

Energies and phonons were calculated for WH’s bcc phase and the \(I4amd\) candidate phase for various pressures. The CASTEP\[9\] code was used with the PBE functional and other settings as used previously\[10, 11, 12\]. Phonon calculations were done using 0.01bohr finite displacements\[13, 14\] with around 3000 k-points per primitive cell, which still introduced a sampling error around 50\(cm^{-1}\). Energy calculations exclude the zero-point energy and pressure.

The \(I4amd\) symmetry can refer to two very different structures depending on the \(c/a\) ratio. Exemplars for this are \(\beta\)–Sn and Cs-IV which have \(c/a\) ratio in the conventional 4-atom cell around 0.6 and 2.2 respectively. For hydrogen the Cs-IV type is generally regarded as most stable\[7\] across a range of exchange correlation functionals\[15, 16\].

There is insufficient detail in the Wigner and Huntington paper to exactly reproduce their calculations, so the data was transcribed directly from Figure 3 in that paper, with units converted to eV and Å\(^3\).

The atomic metallic \(I4amd\) is a stable representative of the free-electron WH phase\[7\], we examined the phonons as a function of pressure. McMahon et al\[17\] have presented the pressure dependence of the \(\Gamma\) point phonons, which were postulated as a match for Phase V Raman data\[18\], however, the validity
of this is unclear, since five non-zero Γ point frequencies are presented from a structure with only two atoms in the primitive cell. Probably they ignored the body centring, an error replicated in Fig 2b.

Although \textit{I}4\textit{amd} is stable with respect to phonon distortions above 250GPa, it develops a fully unstable phonon branch at ambient conditions. Such an instability across the entire Brillouin zone means the structure is unstable to both localised and phonon distortions. Allowing these distortions in molecular dynamics started at 10K takes the structure to an insulating molecular structure within tens of femtoseconds. We do find that the acoustic branches are all positive, consistent with the metastability checks of elastic moduli carried out by Brovman et al.

\textbf{Figure 2.} Phonon dispersion calculated for the WH bcc phase at 0 GPa and for \textit{I}4\textit{amd} metallic hydrogen at 0 and 500GPa. The 0GPa calculation takes the 4 atom tetragonal \textit{I}4\textit{amd} unit cell, while the 500GPa used the primitive cell with the two Raman active modes \textit{Eg} at $1218\pm50 cm^{-1}$ and \textit{B2g} at $2679\pm50 cm^{-1}$. Imaginary frequencies are shown as negative

\textbf{3. Results and discussion}

The graphs of energy and volume show remarkable agreement of the WH calculations and modern DFT. WH calculate that the minimum energy for bcc at $-1.05 R_y, r_s = 1.63 a.u.$ compared to the modern values of $-1.075 R_y$ and $r_s = 1.6834 a.u.$, a level of accuracy not dissimilar to the scatter of modern density functionals. The \textit{I}4\textit{amd} structure is significantly more stable than bcc at all volumes. In fact, WH’s error in choosing bcc rather than \textit{I}4\textit{amd} is larger than that due to their approximations to electronic structure calculation.

To test how long metallic hydrogen remains metastable, a 108 atom supercell of the \textit{I}4\textit{amd} structure was relaxed to ambient pressure while enforcing symmetry, then \textit{ab initio} molecular dynamics was started at 10K in the NVE ensemble. \textbf{Figure 3} shows the evolution of the energy through four distinct phases, 15fs of \textit{I}4\textit{amd} metastability, followed by a further 15fs of molecule formation. We implemented a molecule-finding algorithm which associates each atom with its nearest neighbour, and thereby detects whether a unique definition

\textbf{Figure 3.} Molecular dynamics energy as a function of time for metallic hydrogen, initialized as \textit{I}4\textit{amd} at 10K and 0GPa. Inset shows a snapshot showing molecular liquid after 70fs.
of diatomic molecules exists. After 38fs such a configuration was found. After that some making and breaking of molecules continued up to 100fs, when the material equilibrated as a liquid and temperature had risen to 1000K with a pressure increase of 40GPa. After this the structure was a liquid molecular insulator, with occasional rebonding of the molecules occurring.

4. Conclusion
The predictions of density functional theory for bcc metallic hydrogen are compared with the analytic results obtained by Wigner and Huntington in 1935. The agreement between the two calculations is within a few percent for energy and Wigner-Seitz radius, the compressibility in the two calculations is also similar. This remarkable result seems not to have been properly appreciated, with modern authors still repeating the claim that WH “predicted a transformation at 25GPa”. The difficulty for WH in calculating and accurate transition pressure is that their theory was unable to treat molecular phases on the same footing as the metallic ones. In retrospect, they would have been wise to avoid making any claims about stability.

The elastic stability of the best known candidate structure for the atomic phase, $I 4 amd [7]$, has been investigated. It passes the metastability tests considered by Brovman, having positive acoustic phonons and harmonic elastic moduli at all pressures. However, we find massive optical phonon instabilities leading to molecularization at ambient pressure.

Molecular dynamics provides the answer to Brovman’s issue about the “remains open” lifetime of the recovered state: in the most advantageous case where the depressurization is instantaneous, $I 4 amd$ metallic hydrogen at ambient pressure has a lifetime of order 40fs. The power generated during molecularisation is calculated to be an impressive $10^{17}$ W/mol, but the fuel loading and short release timescale would prove challenging for practical rocketry.

In summary, the predictions of two classic papers on metallic hydrogen at ambient pressure have been reexamined. The energy, volume and compressibility calculated by WH for bcc hydrogen is in remarkably good agreement with DFT calculations. Their prediction that the transition pressure lies somewhere between 25GPa and infinite pressure is also vindicated. The work of Brovman fares less well: although we find that their calculations showing metastability of metallic hydrogen against affine deformation are valid, the stricter criterion of phonon stability is not met. As a consequence, the expected lifetime of putative metallic hydrogen at ambient condition can be measured in femtoseconds.

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[1] Wigner E and Huntington H 1935 J. Chem. Physics 3 764
[2] Brovman E, Kagan Y and Kholas A 1972 Sov. Phys. JETP 35 783–787
[3] Brovman E, Kagan Y, Kholas A and Pushkarev V 1973 Soviet Journal of Experimental and Theoretical Physics Letters 18 160
[4] Brovman E, Kagan Y and Kholas A 1974 Soviet Physics JETP 34 1300
[5] Dias R P and Silvera I F 2017 Science 355 715–718
[6] Pickard C J and Needs R J 2007 Nature Physics 3 473–476
[7] Geng H Y, Song H X, Li J and Wu Q 2012 Journal of Applied Physics 111 063510
[8] Monserrat B, Needs R J, Gregoryanz E and Pickard C J 2016 Physical Review B 94 134101
[9] Segall M, Lindan P J, Probert M, Pickard C, Hasnip P, Clark S and Payne M 2002 Journal of Physics: Condensed Matter 14 2717
[10] Magdă I B and Ackland G J 2013 Phys. Rev. B 87 174110
[11] Ackland G J and Magdă I B 2015 Cogent Physics 2 1049477
[12] Magdă I B and Ackland G J 2017 Phys. Rev. Lett. 118
[13] Frank W, Elssisser C and Fähnle M 1995 Phys. Rev. Lett. 74 1791–1794
[14] Ackland G J, Warren M C and Clark S J 1997 Journal of Physics: Condensed Matter 9 7861
[15] Clay III R C, McMinis J, McMahon J M, Pierleoni C, Ceperley D M and Morales M A 2014 Phys. Rev. B 89 184106
[16] Morales M A, McMahon J M, Pierleoni C and Ceperley D M 2013 Phys. Rev. B 87 184107
[17] McMahon J M and Ceperley D M 2011 Phys.Rev.Letters 106 165302
[18] Dalladay-Simpson P, Howie R T and Gregoryanz E 2016 Nature 529 63–67