Dissipationless quantum states, such as superconductivity and superfluidity, have attracted interest for almost a century. A variety of systems exhibit these macroscopic quantum phenomena, ranging from superconducting electrons in metals to superfluid liquids, atomic vapours, and even large nuclei. It was recently suggested that liquid metallic hydrogen could form two new unusual dissipationless quantum states, namely the metallic superfluid and the superconducting superfluid. Liquid metallic hydrogen is projected to occur only at an extremely high pressure of about 400 GPa, while pressures on hydrogen of 320 GPa having already been reported. The issue to be addressed is if this state could be experimentally observable in principle. We propose four experimental probes for detecting it.

Historically, experimental discoveries of new quantum fluids have often had impact well beyond the physics of condensed matter. The most important quantum fluid states are: 1) superconductivity in metals (1911), 2) superfluidity in $^4$He (1937), 3) superfluidity in $^3$He (1972), 4) high-$T_c$ $d$-wave superconductivity in the copper oxides (1986), and 5) Bose-Einstein condensation of ultracold atoms confined in optical traps (1995). We may also mention recent experiments centered on finding a supersolid state in $^4$He [1], which, if confirmed, would allow crystalline solids to the list of substances with “super” properties along with liquids, vapors and electrons in metals.

Most of these experimental discoveries required novel theoretical ideas for their interpretations, which eventually inspired a number of corresponding novel notions in other branches of physics. A notable example is the seminal work of Bardeen, Cooper, and Schrieffer providing a theory of conventional phonon-mediated superconductivity, which influenced the appearance of the Nambu-Jona-Lasinio model describing dynamical symmetry breaking in particle physics [2]. The phase and spin degrees of freedom in neutral superfluids are naturally related to Goldstone bosons. The Meissner effect in superconductors is a counterpart to the Higgs effect, while the Abrikosov deuterons are spin-one bosons which should likewise lead to Bose condensate with no pairing mechanism required. It was recently demonstrated that once deuterons or protons in superconductors form counterparts to Nielsen-Olesen cosmic strings [3]. There are numerous other examples of deep and intriguing connections between physical phenomena taking place on the macro- and micro-scales [4]. This illustrates rather strikingly how Nature appears to operate on similar principles on vastly different energy- and length scales, and especially how experimental advances in condensed matter physics can indirectly influence and inspire ideas relevant to other branches of physics.

A reasonable question to raise is where further experimental advances in the field of quantum fluids might yet arise. An intriguing possibility, which now appears to be experimentally realizable due to a breakthrough in the synthesis of ultrahard diamonds [5], is the low-temperature liquid metallic state of hydrogen (LMH). As shown originally by Heitler and London, the substantial homonuclear bond in molecular hydrogen owes its existence to the symmetric form of the two-electron wave-function (the spin function being antisymmetric). However, in a condensed state and under the action of compression, the electronic charge density associated with this bond (and corresponding pair potential) is expected to be systematically transferred from the intra-molecular regions, to the inter-molecular regions. A weakening both of the intra-molecular potential and the short-range (repulsive) part of the inter-molecular potential is then anticipated. Since these are the interactions which ultimately lead to spatial order, and since there is a concomitant rise in zero-point energies with compressions, it is also to be expected that the melting point will decline, indeed an effect recently reported by Bonev et al. [6] in very extensive simulations. Further, the continued transference of electron density into the interstitial regions also carries with it the possibility that (exactly as in $^4$He under ordinary conditions) there may be a range of densities where the ordering energies become quite minor compared to zero-point energies. In this situation the result may be a ground-state liquid as the preferred phase. Importantly, it will also be metallic, because densities are sufficient to induce an insulator-metal transition en route. Such a metallic liquid at temperatures of order 100 K is expected to form Cooper pairs of electrons [7]. At lower temperatures also protonic Cooper pairs are expected to form [8]. In liquid metallic deuterium, the deuterons are spin-one bosons which should likewise lead to Bose condensate with no pairing mechanism required.

It was recently demonstrated that once deuterons or protonic Cooper pairs of protons are present along with Cooper pairs of electrons, the resulting “super”-state does not then fall into any class of existing quantum fluids [9].

Two key aspects of this two-component condensate are: (i) It features a superfluid mode of co-directed currents of protons and electrons which supports a superflow of mass but no charge transfer, and a superconducting mode of counter-directed currents of protons and electrons involving dissipationless transfer of charge as well as mass.

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Observability of a projected new state of matter: a metallic superfluid
The neutral superfluid mode does not couple to an external magnetic field, while the charged superconducting mode does. Moreover, the neutral and charged modes are subject to topological constraints originating with condensates that are described by complex scalar fields whose phases should be singlevalued. Thus, topological defects in the form of vortices have a topological charge both in the superconducting and superfluid sectors of the model \[10\]. In this system, superconducting and superfluid properties are therefore inextricably intertwined. This has numerous physical consequences \[8\]-\[11\], one such being that if the system features superconductivity of type-II, then by applying an external magnetic field and controlling temperature, one should be able to drive the system through various topological phase transitions where it can acquire selectively either superconducting or superfluid properties \[9\]. The mechanisms and universality classes of some of these phase transitions have recently been studied in considerable detail \[12\]-\[14\].

A general \(N\)-component mixture of individually conserved condensates at low temperatures should be described by the following \(N\)-component Ginzburg-Landau model, with a free-energy

\[
F = \left\{ \sum_{\alpha,\beta=1}^{N} \frac{1}{2} |(\nabla - i eA)\psi^{(\alpha)}|^2 + V(\{\psi^{(\alpha)}\}) \right\} + F_{A}. \tag{1}
\]

Here, \(F_{A} = \int dr \frac{1}{2} (\nabla \times A)^2\) and the condensate masses \(M^{(\alpha)}\) have been absorbed in the amplitudes \(|\psi^{(\alpha)}|^2 = |\Psi^{(\alpha)}|^2/M^{(\alpha)}|\) for notational simplicity. The condensate order parameters are complex fields denoted by \(\Psi_{\alpha} = |\Psi_{\alpha}| e^{i\theta^{(\alpha)}}\), where \(\alpha = 1...N\), and \(V(|\Psi_{\alpha}|^2) = b_{\alpha}|\Psi_{\alpha}|^2 + c_{\alpha}|\Psi_{\alpha}|^4 + d_{\alpha}|\Psi_{\alpha}|^2|\Psi_{\beta}|^2\). Note the absence of Josephson coupling between different condensate components. This is an important consequence of the fact that each individual condensate is conserved: Cooper-pairs of electrons cannot be converted into Cooper-pairs of protons and vice versa. Moreover, the model Eq. \(1\), where all condensates are taken to be s-wave, should be sufficient to capture the essential physics involved in the four proposed experiments to be described below. We can also exclude pairing of different hydrogenic nuclei when we have very different Fermi momenta. The model in Eq. \(1\) is invariant under change of sign of a charge of any component \((e \rightarrow -e)\) with a simultaneous sign change in phase \((\theta^{(\alpha)} \rightarrow -\theta^{(\alpha)})\). Hence, we can choose the representation where all fields have the same charge sign, but the phase of a positively charged condensate is multiplied by \(-1\). The superfluid properties of the model are then revealed when the variables in Eq. \(1\) are separated into gradients of phase differences which do not couple to the vector potential and represent neutral modes, and a sum of all phases coupled to vector potential which is a charged mode (for details see \[10\], \[15\], \[12\]-\[14\]). Accordingly \(1\) can be rewritten

\[
F = \left\{ \frac{1}{4\Psi^{(\alpha)}_2} \left[ \sum_{\alpha,\beta=1}^{N} |\psi^{(\alpha)}|^2 |\psi^{(\beta)}|^2 \left( \nabla (\theta^{(\alpha)} - \theta^{(\beta)}) \right)^2 \right] + \left( \frac{1}{2\Psi^{(\alpha)}_2} \sum_{\alpha=1}^{N} |\psi^{(\alpha)}|^2 \nabla \theta^{(\alpha)} - e\Psi^{(\alpha)}_2 A \right)^2 \right\} + F_{A}, \tag{2}
\]

where \(\Psi^2 = \sum_{\alpha=1...N} |\psi^{(\alpha)}|^2\). We shall base our discussion below largely on the existence of neutral and charged modes which are explicitly identified in \(2\).

Along with the experimental challenge of achieving the high pressures required to induce hydrogen to take up a liquid metallic state, a central question is whether it is possible to confirm experimentally the very existence of the liquid metallic state itself, i.e. what would be experimentally accessible manifestations in the protonic superconductivity which is expected to coexist with electronic superconductivity at low temperatures. The main difficulties associated with observing such a state are the following: (i) the system is confined in a high-pressure diamond anvil cell of small dimension; (ii) protonic superconductivity cannot be probed even in principle with conventional external electronic contacts simply because protons would not enter the contacts. This rules out resistivity measurements. (iii) Because the critical temperature for electrons is expected to be much higher than that for protons, another standard experimental technique, namely measurement of the Meissner effect, is also inapplicable for detecting protonic superconductivity.

Nonetheless, we will point out several possibilities of experimentally probing and confirming the presence of protonic superconductivity in a high pressure diamond cell containing LMH or a mixture of the hydrogen isotopes. The protonic superconductivity and superfluidity detection experiments suggested below are all based on exploiting the topological properties of the \(U(1) \times U(1)\) or general \([U(1)]^N\) condensate and therefore do not depend principally on microscopic details.

First, we comment on the manner in which a ground-state or near ground-state liquid phase of metallic hydrogen, or deuterium, may be unambiguously identified. Given the recent advances in neutron beam focusing (focused beams as small as 100\(\mu\) are possible at present), direct structural probing (especially for deuterium) from samples confined in diamond cells may be a relatively obvious route. For both hydrogen and deuterium the spin of the neutron might also be usefully engaged in the probing of magnetic order on a span of length scales. Next, we propose four possible experimental probes of protonic superconductivity and superfluidity.

1. Quench induced temperature-dependent fractional magnetic flux. Perhaps the most straightforward method of unequivocally confirming the presence of protonic superconductivity in a diamond anvil cell which might even allow measurement of a protonic gap, is to
produce a multiply connected physical space as shown in Fig. 1, the LMH then occupying a torus. Thermal quench (rapid cooling through the superconducting transition) in a multiply connected space will in general result in non-trivial phase windings of the condensates. This will result in a trapping of quench-induced magnetic flux, given by the expression

$$\Phi = \frac{|\Psi_e(T)|^2}{m_e} n_e - \frac{|\Psi_p(T)|^2}{m_p} n_p - \Phi_0$$  \hspace{1cm} (3)$$

where \(n_{e,p}\) are the quench-induced windings of protonic and electronic condensates phases in units of 2\(\pi\), respectively and \(\Phi_0\) is the magnetic flux quantum. (In general some corrections arising from the Andreev-Bashkin effect might be expected to enter this expression, but they will not alter the picture in any essential way.) Further, if for example, a rapid cooling through the \(T_p\) produces the windings \(n_e = 0, n_p = 1\) then at low temperature the flux would be of order of \(10^{-3}\Phi_0\) which is at least three orders of magnitude larger than the maximum flux resolution in modern experiments. An important point is that the critical temperature \(T_e^c\) for electrons is expected to be much higher than the critical temperature for protons \(T_p^c\). Thus, at temperatures of the order of \(T_p^c\), we have \(|\Psi_e(T)| \approx |\Psi_e(0)|\). The flux will be controlled by the temperature dependent density of the protonic condensate. This should allow a very accurate determination of the temperature dependence of the protonic gap and \(T_p^c\) by measuring the confined magnetic flux quantum. We also stress that thermal quench could be produced by irradiation, illumination and by variation of pressure. For this probe it is not important that the condensates be of type-I or type-II. This technique is also applicable to mixtures of \(N\) condensates. Then, if only the condensate \(\Psi_\gamma\) has a \(2\pi\) phase winding the quench-induced flux will be \(\Phi = \sum_{\alpha = 1}^{N} \frac{|\Psi_\alpha(T)|^2}{m_\alpha} - \frac{|\Psi_\alpha(T)|^2}{m_\alpha} - \Phi_0\).

2. Fractionally quantized magnetic field induced by rotation. The existence of a superfluid mode in the system means that a rotation should produce a vortex lattice in a similar way as in neutral systems, such as rotating buckets of superfluid helium ({}^4He). The fact that a vortex in such a system features both neutral vorticity and carries magnetic flux means that there will be potentially detectable rotation-induced vortices carrying a magnetic flux. We point out that since we are speaking of rotation-induced vortices in a neutral superfluid mode (although the vortices also carry a magnetic flux), for this probe it is also of no importance that the system be a superconductor of type-I or type-II, or even of a mixed type-I/type-II type. A difficulty in realizing such an experiment in presently available diamond anvil cells is their small dimensions and the low mass of electronic Cooper pairs which makes the critical rotation frequency very high. However, we mention a recent breakthrough in fabricating diamonds with large dimensions and fewer defects.

3. Magnetization jump in a transition to a mixed type-I and type-II superconducting state. If both the protonic and electronic condensates at low temperature are type-II superconductors, then the external field measurements might reveal a particular physical signature which is qualitatively different from the behaviour of a single gap system, and which thus can also be used to confirm the presence of a superconducting state of protons. Upon heating the system close to the critical temperature of the protonic condensate, the coherence length for protons should start to diverge while the magnetic penetration length will not vary significantly since it is controlled by the electronic condensate, and given by \(\lambda = 1/e(|\Psi_e|^2/m_e + |\Psi_p|^2/m_p)^{-1/2}\). Thus, there will necessarily exist a temperature range where the coherence length of the protonic condensate will be larger than \(\lambda\). However, in such a situation the vortices can nonetheless be thermodynamically stable. It follows that, if the electrons form a type-II condensate, such a situation may lead to a conversion of the phase transition in an external field from second to first order with a jump of magnetization. The jump in magnetization will be controlled by the non-monotonicity in the interaction between vortices. The longer range attractive part of the intervortex interaction originates with the proton core with the characteristic energy per unit length involved being of order \(E_p^c \times \xi_p^2\), where \(E_p^c\) is the protonic condensation energy and \(\xi_p\) is the protonic coherence length. However, this effect would be eliminated if the system enters a sublattice vortex liquid state at lower temperature, which we expect would be the more likely scenario.
other possibility of detection of a magnetization jump is the following: It is expected that the parameters of the electronic superconductivity could be tuned by applying pressure. In particular, they might possibly be tuned in a wide range from type-I to type-II [6]. If the protonic coherence length at temperatures lower than $T_c^p$ is much smaller than that of the electronic condensate, a pressure-induced crossover from type-II to type-I superconductivity in electrons could conceivably lead to a detection of a magnetization jump. From the magnetization jump and its temperature and pressure dependence one can then extract data on the order parameters.

4. A two-dimensional flux noise probe. If an experiment is conducted in a quasi-2d geometry then this system may undergo a Kosterlitz-Thouless (KT) transition [15] which may be detectable in flux-noise measurements. Flux detection coils have already been effectively utilized in high pressure experiments. In particular small coils can be formed inside artifically grown diamonds and hence such a measurement may also be feasible on LMH, were it to be realized. It is expected that a protonic superconductor will undergo a BEC-BCS crossover with increasing pressure. There will therefore exist a pressure range where the temperature of KT transition temperature would be significantly lower than the temperature of thermal Cooper pair decomposition. An advantage of this particular probe is that the two-component system undergoes a KT transition even in type-I limit [15]. The flux noise measurements in principle yield detailed information on vortex interactions, and therefore also on the possible existence of a composite neutral mode or multiple composite neutral modes in the case of a mixture of hydrogen isotopes [14]. The disadvantage of this method is the necessity of a quasi-2d geometry and the finite sample size limitations that this imposes.

In summary, liquid metallic hydrogen is expected to be realized in diamond anvil cells at pressures of order 400 GPa (currently pressures of around 320 GPa have already been reported on hydrogen [14]). The key issue centers on experimental observability and determining whether or not it is a liquid two-component superconducting superfluid. While standard superconductivity-detection procedures may be inapplicable, we have proposed several alternative experimental probes and also pointed out their limitations. Keeping in mind that precise values of the physical parameters of the projected superfluid state are as yet unknown, we have based our analysis exclusively on topological properties in order to single out effects which are qualitatively different from the case where the system would be a one-component electronic superconductor. The possible experimental probes proposed here show that protonic superconductivity in a high pressure anvil cell is experimentally accessible in principle and therefore these probes should permit an answer to the question of the possible existence of two projected novel states of matter: the metallic and the superconducting superfluids.

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