In the present model, the BEC is a first-order transition just as is the spinless case considered by London.[13]

The work reported here ought to be generalized to include interatomic interactions and the nonuniformity of the magnetic field. One might expect, however, that the basic qualitative results of the present paper would be unchanged.

A basic assumption of this work is that the system is in thermal equilibrium. The following Letter[14] suggests that the relaxation time for the $\nu = 1$ to $\nu = 2$ transition may be long enough that some interesting nonequilibrium effects, involving condensation into the lowest state of each band, may be observable.

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Bose Condensation in Spin-Polarized Atomic Hydrogen

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A phenomenological description of spin-polarized hydrogen is proposed in terms of two Bose fields which correspond in the low-density limit to the two lowest atomic hyperfine states. Experiments should initially populate both states and the equilibration time of the relative population will be long. When Bose condensation occurs in both states, a spontaneous coherent magnetization perpendicular to the stabilizing field will appear that may be observable in a magnetic resonance experiment.

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A number of authors have suggested that atomic hydrogen would be an interesting bosonlike quantum fluid at low densities and temperatures.[1] It became obvious that to stabilize the atoms against recombination into molecules, an external magnetic field was needed although for any field attainable in the laboratory the atomic state will still be only metastable.[2] The calculation of precise recombination rates is a difficult problem in chemical physics that has not been quantitatively settled.[3,4] Recent experiments have provided some hope that long-term stabilization may be possible,[5] so that it seems worthwhile to inquire how the Bose condensed states might be observed.

Here a number of seemingly awkward aspects of spin-polarized hydrogen, ($H\uparrow$), as contrasted with ^4He, work to our advantage. We shall see that $H\uparrow$ is expected to act in many ways like a spin-$\frac{1}{2}$ Bose fluid with a magnetic moment several times the proton's. The stabilizing field is ready made for a magnetic resonance experiment[6] that is noninvasive and can be done on a much shorter time scale than the traditional superfluid flow experiments. In this paper we will suggest one possible experiment and outline the phenomenology necessary to study quantitatively the low-temperature phases of H↑ in an idealized bulk sample.

Atomic hydrogen in its orbital ground state can exist in four hyperfine states. In a large field, that we will henceforth take as 10 T, these states are, in order of increasing energy,

$$\begin{aligned} |a\rangle &= (|-+\rangle - \epsilon|+-\rangle)/(1+\epsilon^2)^{1/2}, \\ |b\rangle &= |--\rangle, \\ |c\rangle &= (|+-\rangle + \epsilon|-+\rangle)/(1+\epsilon^2)^{1/2}, \\ |d\rangle &= |++\rangle. \end{aligned} \tag{1}$$

The parameter ϵ is approximately $a/2\mu_e H_z \sim 2 \times 10^{-3}$, where a is the hyperfine interaction constant, μ_e is the magnitude of the electron magnetic moment, and H_z the stabilizing field. Within each ket, the two signs refer to the direction of the electron and proton spins, respectively.

On physical grounds, the small parameter that permits us to use Bose statistics for a given hyperfine state is the ratio of a typical kinetic energy, E_k, to an atomic binding or excitation energy, E_b. This is equivalent to requiring that the atomic number density, n, be much less than an inverse atomic volume as can be seen by replacing E_k in the above ratio by the Fermi energy of the electrons thought of as free. To the extent that E_k/E_b is small, a many-particle wave function antisymmetric under interchange of fermions can be rewritten as a symmetric combination of atomic states with each electron paired with a proton. While it is certainly plausible to treat H↑ as a boson under the anticipated experimental conditions, we are unable to rule out that the composite nature of the putative bosons might not be manifest in some subtle way below the λ transition.

For concreteness, let us consider the following microscopic Hamiltonian:

$$H = H_0 + \tfrac{1}{2}\sum_{ij} V_D(r_{ij}) + \tfrac{1}{2}\sum_{ij} V_E(r_{ij}) \vec{S}_i \cdot \vec{S}_j, \tag{2}$$

where H_0 includes the kinetic and intra-atomic energies as well as the interaction with the external field.[7] The electron spin is denoted by S, and $V_D = \frac{1}{4}(V_S + 3V_T)$, $V_E = V_T - V_S$, where V_T and V_S are the well-known triplet and singlet potentials between hydrogen atoms.[8] We have temporarily omitted a number of small terms involving the magnetic dipole interaction between electrons and protons on different atoms.[9]

Equation (2) can now formally be rewritten in terms of the four second-quantitized boson field operators $\Psi_a, \ldots, \Psi_d$ corresponding to the atomic states in (1). Within the a-b subspace, the effective potential consists of a term essentially equal to V_T that acts on the total density and a smaller term of order $\epsilon^2 V_E$ that acts on the "spin" density $\frac{1}{2}\Psi^+ \tau_i \Psi$, where Ψ^+ is the spinor (Ψ_a^+, Ψ_b^+) and τ_i $(i = x, y, z)$ are the Pauli matrices $(\tau_i^2 = 1)$. Thus, one contribution to the transverse relaxation time, T_2, is, roughly, $h/\epsilon^2 J_0$, where J_0 is the average of V_E over a pair distribution function determined by V_T.[7] The interactions in (2) cannot relax the total z spin, so that the crudest possible estimate of the thermalization time, T_1, of the relative populations, $n_a - n_b$, due to the electron-proton dipole interaction gives $T_1 \sim 10$ min.[10] Note that (2) can mix states $|a\rangle$ and $|c\rangle$ in (1).

Any discussion of H↑ at low temperatures should include two boson states whose spin dependence reduces to $|a\rangle$ and $|b\rangle$ at low densities. Physically, the antiferromagnetic exchange in (2) enhances the small electron spin-up piece of $|a\rangle$. The energy difference between the atomic states a and b is only 54 mK at $H_z = 10$ T. Even if our estimate of T_1 is badly in error, this time will still be much longer than the thermalization time of a Bose condensate in either spin state which is set by V_T. Thus, magnetic resonance could be used to populate b and thereby the effects we propose below should be rendered observable.

At finite temperatures and long wavelengths, the competition between the antiferromagnetism and the external field can be treated classically. No long-range order develops in the staggered magnetization, N, if $J_0/\mu_e H_z$ is sufficiently small. Antiferromagnetic correlations should promote recombination.[3,7] In what follows, we will set $N = 0$ and note that the shallow minimum in $V_T(r)$ at $r \sim 4.14$ Å will not bind a pair of atoms.[8]

To study the low-temperature phases of H↑ phenomenologically, we will follow Penrose and Onsager[11] and define $|a\rangle$ to be the total z-spin-zero state with off-diagonal long-range order. Berlinsky's calculation[7] suggests that the atomic value of ϵ in (1) is multiplied by $\mu_e H_z/(\mu_e H_z - J_0)$ at low temperatures. We will retain ϵ as a parameter that is experimentally accessible through $\mu_\perp$ defined below. Because Ψ_a, Ψ_b refer to internal states of the same particle, we can superimpose them and write the operator representing the magnetization density, m_i, as $\frac{1}{2}\mu_i \Psi^+ \tau_i \Psi$, where

$$\mu_{x,y} \equiv \mu_\perp = \mu_p + \epsilon \mu_e\,, \quad \mu_z = \mu_p - \epsilon^2 \mu_e\,. \tag{3}$$

We have neglected in m_z a background piece proportional to the total density.

Although a good deal can be done microscopically, we have found the structure of the theory both above and below the Bose-condensation temperature to be more clearly presented phenomenologically.[12] Let the free energy be

$$F = \int d^3x \left(\tfrac{1}{2} r |\Psi|^2 + \tfrac{1}{4} u |\Psi|^4 + \textstyle\sum_i \tfrac{1}{2} \gamma \sigma_i \Psi^+ \tau_i \Psi + \tfrac{1}{2} \sigma_z^2 / x_z + \tfrac{1}{2} \sigma_\perp^2 / x_\perp - H_z \mu_z \sigma_z\right). \tag{4}$$

With $\hbar = 1$ the equations of motion read

$$\frac{\partial \Psi}{\partial t} = \frac{i}{2} \sum_i \frac{\delta F}{\delta \sigma_i} \tau_i \Psi - 2\Gamma \frac{\delta F}{\delta \Psi^+}\,, \tag{5a}$$

$$\frac{\partial \sigma_i}{\partial t} = \mathrm{Im}\left(\frac{\delta F}{\delta \Psi} \tau_i \Psi\right) + \left(\vec{\sigma} \times \frac{\delta F}{\delta \vec{\sigma}}\right)_i - T_2^{-1} \frac{\delta F}{\delta \sigma_i} (1 - \delta_{i,z}). \tag{5b}$$

All fields are now classical but have the same meaning as their quantum analogs, i.e., Ψ is the spinor order parameter for the Bose condensation. The vector "spin" density is denoted by $(\sigma_\perp, \sigma_z) = (m_\perp/\mu_\perp, m_z/\mu_z)$, $\gamma \approx 1$, and the anisotropic g factors, (3), have been absorbed into the corresponding susceptibilities $\chi_\perp, \chi_z$. As before, a background spin proportional to the total density has been dropped. We have omitted the customary gradient terms from (4) and the Langevin model of thermal noise from (5) since they are not needed in what follows. Phenomenologically, densities are not simply expressible in terms of the classical order parameter since we imagine that short-wavelength quantum and thermal fluctuations were integrated out to arrive at (4)–(5). For $i = x, y$, (5b) reduces essentially to Bloch's equations; the order parameter enters only the relaxation term. For $i = z$, we have assumed $T_1^{-1} = 0$, so that (5b) becomes $d\sigma_z/dt = 0$.

Following Ginzburg-Landau theory, we imagine that r becomes negative (with $u > 0$) as the temperature is decreased, so that if σ_z is sufficiently small and fixed, Bose condensation will occur successively in both states a and b.[13] The low-temperature order parameter is characterized by two phases φ_a and φ_b. The hydrodynamics of the doubly condensed state was considered in Ref. 14 (neglecting electromagnetic effects). One novel feature of the superfluid hydrodynamics is a cross superfluid density $\rho_s^{a,b}$ whereby a phase twist in one component induces a mass current in the other. This effect would follow from (4)–(5) if we included in (4) a term proportional to $(\nabla\sigma_\perp)^2$ and then integrated out $\sigma_\perp$ or let it relax on the grounds that $\sigma_\perp$ is *not* a hydrodynamic variable. The residual antiferromagnetic interactions make a negative contribution $\rho_s^{a,b}$ and we will assume for stability that $(\rho_s^{a,b})^2 < \rho_s^a \rho_s^b$.

The magnetic properties of the condensed system with long-range order in both states a and b are quite interesting since the perpendicular magnetization acquires a spontaneous value $\mu_\perp \sigma_\perp$ of order $\mu_\perp (n_a^0 n_b^0)^{1/2}$ in physical units, where $n_{a,b}^0$ are the condensate densities. Microscopically, $\mu_\perp \sigma_\perp$ is the expectation value of the operator $m_{x,y}$, defined above (3), in a broken symmetry ensemble. The spontaneous magnetization is coherent over the sample and its direction in the x-y plane is determined by $\varphi_a - \varphi_b$. When the system is prepared such that σ_z does not equal its thermal equilibrium value, $\sigma_\perp$ will rotate at a frequency corresponding precisely to the chemical potential difference between particles in states a and b.

Let us schematically represent the environment of a superfluid sample of H↑ by a resonant coil of inductance L and resistance R, oriented along the x direction, and connected in parallel with a capacitance C. Imagine that the populations n_a and n_b are nonthermal; then the time variation of $\sigma_\perp$ will induce a current in the coil at precisely the frequency necessary to induce magnetic resonance between states a and b. The coil then produces a magnetic field in the x direction that should be added to the Bloch equations for σ_z and σ_y in the conventional manner. When $R = 0$, energy is exchanged reversibly between the coil and the sample. In practice, we suspect that R will set the thermalization time of $n_a - n_b$, although true radiative damping is also a possibility. Of course, as the populations relax, the resonance frequency will change. At a finite temperature, n_b^0 may decrease to zero as σ_z increases before thermalization is complete. A microscopic calculation of T_1 then becomes necessary.

There is a significant difference between magnetic resonance in Bose-condensed H↑ ($T_1^{-1} = 0$)

and an ordinary fluid that is illustrated by the effects of an inhomogeneous field. In thermal equilibrium, the chemical potential (μ_a and μ_b separately in H$\uparrow$) must be uniform. The Josephson relation[15] applied to H$\uparrow$ implies that $\sigma_\perp$ rotates with a frequency $(\mu_a - \mu_b)/\hbar$. On the other hand, in an ordinary fluid the rotation rate is set by the local field. This is only slightly modified by the magnetostriction induced by the external field gradient and thus an inhomogeneous broadening is to be expected in the fluid but not in H$\uparrow$.

Our discussion until now has assumed a single-domain sample with respect to $\sigma_\perp$. The demagnetizing fields that result from inclusion of the dipolar forces are of order $\mu_\perp n \sim 10^{-8}$ T, for $n \sim 10^{19}/\text{cm}^3$, and are therefore quite tiny compared to those in conventional ferromagnets. The stiffness constant opposing a change in the direction of $\sigma_\perp$ is of order $\rho_s{}^b\hbar^2/m_p{}^2$, where m_p is the proton mass. There is no anisotropy energy to limit the size of domain walls. Energetic arguments suggest that $\sigma_\perp$ will vary smoothly on a scale of 10^{-1} cm. The formation of domains requires nonzero supercurrents to exist in thermal equilibrium ($T_1{}^{-1} = 0$). The morphology of domains is sufficiently complex that we hesitate to make predictions about real experiments other than to suggest the use of a small rotating x-y field to overwhelm the demagnetizing fields estimated above.

We do not expect any direct analog in H$\uparrow$ to the coherent dipole or spin-orbit energy that is responsible for the longitudinal resonance in superfluid ^{3}He.[16] That effect arises from the nuclear dipole-dipole interaction between two ^{3}He nuclei whose spatial wave function is simultaneously correlated via the Cooper pairing. Bose condensation does not result in any particular directional correlation in atomic positions.

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