[7]See, for example, J. Wilks, *Liquid and Solid Helium* (Clarendon, Oxford, England, 1967).

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[9]R. C. Dynes, private communication. See also Fig. 29 and related discussion in Ref. 2.

Possible "New" Quantum Systems

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Systems of spin-aligned hydrogen isotopes are studied. They are shown to exhibit even more extreme "quantum" behavior than the helium isotopes. Spin-aligned hydrogen is predicted to be a gas at *all* temperatures and its Bose-Einstein condensation and possible superfluidity are discussed. Spin-aligned deuterium is predicted to show critical behavior strongly influenced by quantum mechanics. The preparation of spin-aligned hydrogen (in the presence of large magnetic fields) is also discussed.

Recently Dugan and Etters[1] and Etters, Dugan, and Palmer[2] have studied the ground-state properties of spin-aligned isotopes of hydrogen, which we denote by H↑, D↑, and T↑. They used a Morse-potential approximation to the accurate pair potential for two hydrogen atoms in the $b\,^3\Sigma_u^+$ state calculated by Kolos and Wolniewicz.[3] DEP pointed out that systems composed of these spin-aligned atoms were strongly quantum mechanical systems analogous to those composed of the helium isotopes and they briefly discussed their possible superfluidity.

Here we discuss further these spin-aligned systems which may conceivably be prepared in magnetic fields of the order of 10^5 G. Our main point is that the study of these systems should yield exciting and fundamental new information about the properties of quantum systems. Since H↑ and D↑ are lighter and more weakly interacting than ^{4}He or ^{3}He, they may be expected to exhibit even more extreme quantum behavior than helium does. The present work utilizes recent studies of quantum systems within the context of the quantum theorem of corresponding states (QTCS).[4-6] We analyze the expected superfluid properties and the quantum-mechanically driven phase transitions which may occur in these systems.[4,5] We also discuss briefly the feasibility of preparing spin-aligned systems.

We shall begin with a discussion of the K-W potential for the $b\,^3\Sigma_u^+$ state of H_2 (Fig. 1). We have also pictured a Lennard-Jones (L-J) potential chosen to fit the well depth and position of the minimum of the K-W potential. Although DEP fit the K-W potential with a Morse potential, we believe that the L-J potential also gives a reasonable fit. Moreover, it represents the long-range r^{-6} part of the potential better, which is important for these weakly bound systems. In addition, it allows us to make contact with the wide range of calculations which already exist for L-J systems.[4,5]

We now recall briefly the QTCS.[7,4] It applies to a class of systems with a pair potential of the form $v(r)=\epsilon v^*(r/\sigma)$ where ϵ is the coupling constant, σ is the "collision diameter," and $v^*(x)$ is the same dimensionless function for each system in this class. For the L-J potential, $v^*(x)=4(x^{-12}-x^{-6})$. We introduce the quantum parameter[4] $\eta \equiv \hbar^2/m\epsilon\sigma^2$, the reduced temperature $T^*=k_BT/\epsilon$, the reduced volume $V^*=V/N\sigma^3$, and the reduced Helmholtz free energy $F^*=F/N\epsilon$. The QTCS states that for a one-component system, $F^*=F^*(T^*, V^*, \eta)$, where F^* depends *only* on the form of $v^*(x)$ and on whether the particles obey *Bose-Einstein* or *Fermi-Dirac* statistics.[7,4] Values of ϵ, σ, η, and other useful quantities are given in Table I for H↑, D↑, T↑, and other light elements. Heavier spin-aligned atoms such as Li↑ and N↑ are not expected to show significant

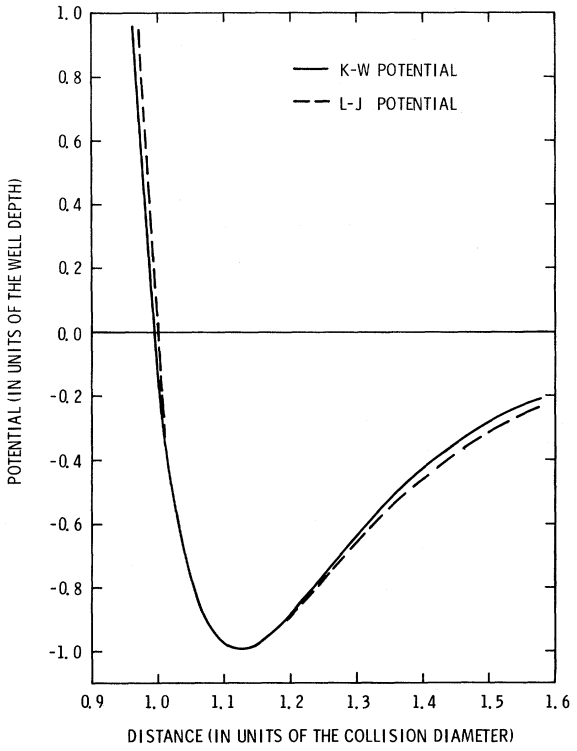

FIG. 1. Graph of the K-W potential for the $b\,^3\Sigma_u^+$ state of H_2. Also shown is a graph of the L-J potential chosen to fit the well depth (4.492 cm^{-1}) and minimum distance (4.141 Å) of the K-W potential.

quantum behavior.

Let us now consider H↑, which is expected to obey *Bose-Einstein* statistics. This system is predicted to be a gas in its ground state[1,2,8] and at *all* temperatures as found by MNP, since its value of η is much greater than the critical value η_c

TABLE I. The quantum parameter η for various substances. Also included are the masses (in amu, i.e., $1.660\,24\times10^{-24}$ g), the coupling constants ϵ (in deg, $k_B = 1.38054\times10^{-16}$ erg/particle deg), the "core diameters" σ (in Å), and $N_0\sigma^3$ (in cm^3/mole). We used $\hbar = 1.054\,50\times10^{-27}$ erg sec and $N_0 = 6.022\,52\times10^{23}$ particle/mole.

Substance	m	ϵ	σ	$N_0\sigma^3$	η
H↑	1.008	6.46	3.69	30.2	0.55
D↑	2.014	6.46	3.69	30.2	0.27
T↑	3.016	6.46	3.69	30.2	0.18
^{3}He	3.016	10.22	2.556	10.06	0.2409
^{4}He	4.003	10.22	2.556	10.06	0.1815
^{6}He	6.019	10.22	2.556	10.06	0.1207
H_2	2.016	37.0	2.92	14.99	0.0763
D_2	4.028	37.0	2.92	14.99	0.0382

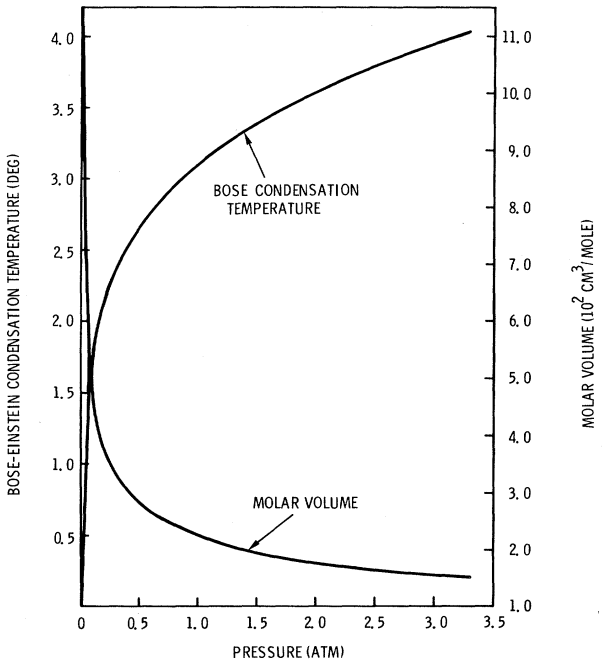

FIG. 2. Graph of the *Bose-Einstein* condensation temperature and molar volume of a Bose gas with $\eta = 0.55$ versus pressure.

$\simeq 0.45$ which they found. In Fig. 2 we have plotted the molar volume and the Bose-Einstein condensation temperature[9] for an ideal Bose gas (T_{BE}) as functions of pressure.[10] Clearly there as easily accessible regions of temperature and pressure where the molar volume is very large; therefore, this system is expected to be a nearly ideal *Bose-Einstein* gas! Thus, it would clearly be an important and exciting experiment to try to study the *Bose-Einstein* condensation in H↑.

It is our opinion that the study of the Bose-Einstein condensation is the most important experiment that can be done with H↑. After all, at the present time there is really no fundamental understanding of the λ transition in ^{4}He. It is not even possible to state categorically that the Bose gas *will* be superfluid below T_{BE}. There could, conceivably, be a superfluid transition at a lower temperature. If the gas does become superfluid at T_{BE}, the study of this transition will undoubtedly be extremely important for our understanding of Bose systems and their superfluidity.

Let us now consider D↑, which is expected to obey Fermi-Dirac statistics. The results of DEP suggest that D↑ will also be a gas at zero temperature, although they did not explore very large molar volumes and their potential did not have the proper r^{-6} long-range behavior. MNP found

that for $\eta \gtrsim 0.27$, a Fermi system would be a gas at zero temperature, whereas for $\eta \lesssim 0.27$ it would be a liquid. Thus, D↑ is a borderline case so that a more accurate calculation using the true potential would be worthwhile. MNP also found that for $0.27 \lesssim \eta \lesssim 0.31$, a Fermi system would have coexisting gas and liquid phases at zero temperature and proper pressure. Thus, it may be that D↑ is the only system which has an η in this interesting coexistence region. Extrapolations of the curves for T_c* and V_c* versus η given in Figs. 3 and 5 of Ref. 6 indicate that $T_c \simeq 1.2$ K and $V_c \simeq 230$ cm^3/mole for D↑. As indicated by MNP, it is likely that this critical region would be dominated by quantum effects ("quantum condensation"). Thus, in this case it might be possible to observe quantum effects on the critical exponents. As a final point, we mention that superfluidity in D↑ should be very much like that of ^{3}He in a strong field.

We may also discuss briefly the solidification of H↑ and D↑. By extrapolating the results of NPP, we find that H↑ should solidify at $P_s \simeq 50$ atm with $V_s \simeq 65$ cm^3/mole; D↑ should solidify at $P_s \simeq 8$ atm with $V_s \simeq 75$ cm^3/mole. It may be more difficult to observe the solidification because of the relatively high densities of the solid phases. As far as T↑ is concerned, we shall comment only that it should be very much like ^{4}He.

Should it be possible to prepare these spin-aligned species, there are many other experiments for which they could be utilized; e.g., mixture of these species with each other and with helium.[6] These species could be used as probes of properties of helium that are not fully understood, such as the λ transition, vorticity, and the propagation of impuritons in solid He.[11] It should be noted that these solids should be *nonmetallic* at pressures small compared to megabars. We should also emphasize that various resonance techniques could be utilized in these spin-aligned systems.

Finally, we wish to discuss briefly the experimental feasibility of preparing macroscopic samples of H↑, D↑, or T↑. Hess and Peschka[12] have obtained evidence for condensed D↑, but with considerable D_2 also present. In these experiments, the output of a discharge (D and D_2) was condensed at 1.4 K in a 60-kG magnetic field, so that the Zeeman splitting between electronic levels was large compared to kT. They concluded that the magnetic field considerably enhanced the amount of D atoms which can be stabilized (for hours) in a condensed phase. If we accept this work, we may conclude that the recombination time for D atoms is indeed very long at 1.4 K and 60 kG.

To produce condensed H↑ or D↑, a beam of these atoms could be utilized; the production of fluxes up to 0.001 mole/sec has now been achieved.[13] These atoms could either be fed directly into an experimental region[12] or they could be preselected,[14] e.g., by an inhomogenous hexapole magnet. Once in the experimental region, surface effects are likely to be important. It is to be expected[15] that, under most conditions, hydrogen atoms will build up on the surface of the experimental area; the H-surface forces are strong relative to the H↑-H↑ forces. After a layer or two of H↑ has been deposited, it may be possible to maintain H↑ in the gas phase for significant periods of time. The dominant loss process might be expected to be electronic spin flip, which leads to H_2 formation. The existence of a hydrogen maser is evidence that spin-flip processes are slow at room temperature; additionally, the Hess-Peschka results[12] suggest that they are also slow at 1.4 K. Clearly, high magnetic-field-to-temperature ratios tend to suppress them, just by energy conservation. Jones *et al.*[16] estimated a ratio of approximately 10^5 G/K was needed. Thus, there are good reasons to believe that it may be possible to prepare macroscopic systems of spin-aligned hydrogen, at least in the gaseous phase. Thus, we believe that an experimental research program directed towards this end is fully warranted, and, if sucessful, could lead to a substantial increase in our basic understanding of quantum systems.

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Uniaxial Stress Effect on the Electron Affinity of the D^- State in Germanium

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Long-wavelength (submillimeter plus millimeter) photoconductivity measurements in doped germanium have been performed under uniaxial compressive stress along the [111] crystal direction. The electron affinity estimated from newly observed spectra is smaller than that in a previous measurement without stress and is consistent with the theoretical prediction for the D^- state. The larger electron affinity of the D^- state without stress is ascribed to a many-valley effect.

Though many experimental results[1-6] associated with the impurity states in semiconductors have been ascribed to the D^- (or A^+) states, conclusive evidence of the existence of the D^- (A^+) state has not been reported. In the submillimeter photoconductivity measurements on Ge,[6] the experimental electron affinity of the shallow trapping state, which has been supposed to be the D^- state, was about 3 times larger than the theoretical value[7] estimated by a simple analogy to H^-.[8] Moreover the spectral shape of the photoconductivity does not agree with the theoretical one. Even if the existence of the D^- state in Ge (or Si) is assumed, the complete analogy of it with H^- would not hold, because the conduction band in Ge (Si) has many-valley structure with anisotropic energy surfaces.

In this Comment we wish to report a stress experiment on the long-wavelength (submillimeter plus millimeter) photoconductivity in Ge, performed in order to reduce the many-valley structure to the single-valley one. By this experiment, we have confirmed that the mentioned discrepancy between experiment and the theory comes mainly from the effect of the many-valley structure in Ge, and we believe our results to be the first conclusive evidence for the existence of the D^- states in semiconductors.

The present photoconductivity measurements are performed on Sb-doped germanium crystals under uniaxial compressive stress along the [111] crystal direction by the use of a lamellar grating spectrometer and extending the wavelength range from submillimeter to millimeter. By applying a [111] stress, the four conduction-band valleys in germanium become inequivalent in energy; that is, the energy of the valley with the principal axis of the energy ellipsoid parallel to the [111] stress direction is lowered, while the other three valleys are equally elevated in energy. Thus, under sufficient stress, the electrons in the four valleys are accumulated into the lowest [111] valley and the crystal behaves as a semiconductor with a single conduction-band val-