MAGNETIC RESONANCE STUDIES
OF ATOMIC HYDROGEN GAS
AT LIQUID HELIUM TEMPERATURES

by

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B.Sc., University of British Columbia, 1977

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE

in

THE FACULTY OF GRADUATE STUDIES
DEPARTMENT OF PHYSICS

We accept this thesis as conforming

to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA

November, 1979

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Pulsed magnetic resonance studies are reported for a gas of hydrogen atoms at densities of \(3-10 \times 10^{13} \text{ cm}^{-3}\) and temperatures of 4.2-77 K. The gas was produced by dissociation in a room temperature R.F. discharge, and piped through glass tubing into the cryogenic apparatus for study. The magnetic resonance transition observed is between the two lowest hyperfine levels of the 1s atom in a magnetic field of 6481 Gauss where this splitting has its minimum value of about 765.5 MHz.

At 77 K, spin-exchange broadening of the resonance is observed. By varying the number density of hydrogen atoms, the ratio of spin-exchange broadening to atomic hydrogen density is obtained, and from this ratio the spin-exchange cross section for this transition is calculated. The cross section obtained is 60\% of the theoretical value.

At liquid helium temperatures, the spin-exchange cross section is shown to be at least 15 times smaller than that at liquid nitrogen temperatures, as predicted by theory. He\(^4\) and H\(_2\) buffer gases are used to limit the diffusion broadening of the resonance, allowing the observation of small frequency shifts of the free induction signal. A model is proposed in which interactions of the hydrogen atoms with the flow tube walls cause these shifts. From the diffusion broadening of the resonance, the diffusion cross sections for H in He\(^4\) at 4.2 K and H in H\(_2\) at 5-9 K are inferred to be 500 \(\text{Å}^2\) and 250 \(\text{Å}^2\) respectively.
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ACKNOWLEDGEMENTS

I would like to acknowledge the support of Dr. A. J. Berlinsky in the supervision of this project. I have also benefited greatly from the help and advice of Dr. W. N. Hardy. Finally I wish to thank the National Sciences and Engineering Research Council of Canada for a Postgraduate Scholarship.
CHAPTER I  INTRODUCTION

The hydrogen atom, by virtue of its simplicity, has long been the subject of very precise tests of physical theories. By analogy one might wonder whether macroscopic quantities of atomic hydrogen could provide for the theory of condensed matter what the isolated atom provides for quantum electrodynamics - an ideally simple experimental material. Unfortunately, this does not seem to be the case, mainly because atomic hydrogen is chemically unstable - reacting to form $H_2$. Atomic H at high densities is therefore not a simple system, and presents formidable experimental difficulties.

Recently, however, interest has developed in the possibility of preventing the recombination of H into $H_2$ by the application of a very strong magnetic field (of order 100 KG) at very low temperatures (of order .1 K)$^{1-4}$. Under these conditions the electron spins are nearly 100% polarized, and the fact that the triplet-state pair potential for hydrogen atoms is mainly repulsive is expected to prevent recombination.

Since the hydrogen atom is a bound state of two fermions, it is a Bose particle, and it might therefore be possible to observe Bose-Einstein condensation in spin polarized atomic hydrogen. For non-interacting particles, the temperature for Bose-Einstein condensation is

$$T_{BE} = \left( g_{\frac{3}{2}} \right)^{-2} \frac{2\pi \hbar^2}{k m} n^{\frac{3}{2}} \approx (1.527) \frac{2\pi \hbar^2}{k m} n^{\frac{3}{2}}$$  \hspace{1cm} (1.1)

where $g_{\frac{3}{2}} = \sum_{l=1}^{\infty} l^{-3/2}$

and $m$ and $n$ are the mass and number density of the particles.
For $T_B = .1$ K, the density required for non-interacting particles with the mass of a hydrogen atom is $1.6 \times 10^{19}$ cm$^{-3}$, which is much smaller than the density of $2.3 \times 10^{22}$ cm$^{-3}$ for the superfluid transition in liquid helium. It is hoped that Bose-Einstein condensation in spin-polarized atomic hydrogen might occur at such low densities, in which case the effects of interactions between the atoms would be much smaller than in the case of superfluid helium. The system would thus provide a very good test of the theory of Bose-Einstein condensation.

To date very little experimental work has been done on atomic hydrogen gas at low temperatures, although at room temperature a large amount of work has been done on the (atomic) hydrogen maser, and data on H-atom recombination$^6$ and spin-exchange broadening of magnetic resonances$^7$ have been obtained down to liquid nitrogen temperature. The experimental work reported here has been motivated by the need for information on the properties of atomic hydrogen at low temperatures which are relevant to the production and study of spin-polarized atomic H.

Pulsed magnetic resonance was used to detect hydrogen atoms at liquid helium temperatures and liquid nitrogen temperature. (This experiment$^8$, as well as that of Crampton et al.$^9$, is the first use of magnetic resonance on atomic hydrogen at liquid helium temperatures). Although there are simpler methods of detecting atomic hydrogen (such as recombination detectors which catalyze recombination of H into H$_2$ and measure the resultant heat production), magnetic resonance was employed
because it is extremely specific. The H-atom resonance frequency can be both calculated and measured to better than 1 in 10^7. In addition the magnetic resonance signal provides information about the interactions of H-atoms with one another, about their diffusion, and about their recombination rate - precisely the type of information needed for future "spin-polarized" atomic hydrogen studies.

In Chapter II of this thesis, the derivation of the hyperfine levels of the ls hydrogen atom in a magnetic field is presented, and the technique of pulsed magnetic resonance is discussed. Chapter III deals with the practical problem of producing hydrogen atoms in a discharge, and discusses the discharge apparatus used in this experiment. Chapter IV contains a description of the pulsed magnetic resonance system, and the novel resonator employed. In Chapter V, the over-all experimental design is discussed, with emphasis on the cryogenic, gas handling, and magnetic field measurement techniques. Finally, Chapter VI is a presentation of the experimental results and their analysis.
CHAPTER II  THE HYPERFINE LEVELS OF THE 1S STATE HYDROGEN ATOM

2.1 Calculation of the Energy Eigenvalues.

The Hamiltonian for the spin degrees of freedom of the 1s hydrogen atom is

$$H = a \mathbf{I} \cdot \mathbf{S} - 2H \mu_p I_z + 2H \mu_e S_z$$

(2.1)

where $H$ is the magnitude of the magnetic field (which is in the positive z direction), $\mu_p$ is the proton magnetic moment ($\mu_p = 1.41 \times 10^{-23}$ erg/Gauss), $\mu_e$ is the electron magnetic moment ($\mu_e = 9.27 \times 10^{-21}$ erg/Gauss), $\mathbf{I}$ and $\mathbf{S}$ are the proton and electron spin operators, and $a$ is the hyperfine coupling constant ($a = 9.41 \times 10^{-18}$ erg).

It is convenient to work in the basis in which $I_z$ and $S_z$ are diagonal. The basis states will be represented as $|\uparrow\uparrow\rangle$, $|\uparrow\downarrow\rangle$, $|\downarrow\uparrow\rangle$, $|\downarrow\downarrow\rangle$, where $\uparrow$ or $\downarrow$ refer to the electron spin being up or down, and $\uparrow$ and $\downarrow$ refer similarly to the proton spin. In this basis, the matrix representation for the operators appearing in the Hamiltonian are:

$$I_z = \frac{1}{2} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$

(2.2)
and thus the representation of the Hamiltonian is

\[
S_z = \frac{1}{2} \begin{pmatrix}
1 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 \\
0 & 0 & -1 & 0 \\
0 & 0 & 0 & -1
\end{pmatrix} (\uparrow \uparrow) (\uparrow \downarrow) (\downarrow \uparrow) (\downarrow \downarrow)
\]

\[
\frac{\hbar}{\sqrt{2}} S_z = \frac{1}{2} \begin{pmatrix}
1 & 0 & 0 & 0 \\
0 & -1 & 2 & 0 \\
0 & 2 & -1 & 0 \\
0 & 0 & 0 & 1
\end{pmatrix} (\uparrow \uparrow) (\uparrow \downarrow) (\downarrow \uparrow) (\downarrow \downarrow)
\]

It is immediately evident that the states \( |\uparrow \uparrow \rangle \) and \( |\downarrow \downarrow \rangle \) are also eigenstates of this Hamiltonian, with energy \( H(\mu_e - \mu_p) + a/4 \) and \( -H(\mu_e - \mu_p) + a/4 \) respectively. These are states 4 and 2 as shown in Fig. 2.1. After some straight-forward algebra, it is found that the other two
Figure 2.1 Hyperfine levels of the $1s$ hydrogen atom as a function of magnetic field.
eigenvalues shown in Fig. 2.1 are

\[ E_1 = -\frac{a}{4} - \sqrt{\frac{a^2}{4} + H^2 (\mu_e + \mu_p)^2} \]  
(2.4)

\[ E_3 = -\frac{a}{4} + \sqrt{\frac{a^2}{4} + H^2 (\mu_e + \mu_p)^2} \]  
(2.5)

with eigenstates

\[ \psi_1 = \cos \theta \left| \uparrow \uparrow \right\rangle - \sin \theta \left| \uparrow \downarrow \right\rangle \]  
(2.6)

\[ \psi_3 = \sin \theta \left| \uparrow \uparrow \right\rangle + \cos \theta \left| \uparrow \downarrow \right\rangle \]  
(2.7)

where

\[ \tan 2\theta = \frac{a}{2} (\mu_e + \mu_p) H \]  
(2.8)

At zero field, three of these states, (2,3,4), are degenerate, and are the three \( J=1 \) eigenstates of the total spin operator \( J = I + S \), while the other, (1), has total spin 0. The energy difference, \( a \), between state 1 and 2, 3, or 4 can be calculated fairly accurately from the electronic wave function and quantum electrodynamics \( ^{10} \), and has been measured to 2 parts in \( 10^{12} \) by means of the hydrogen maser which operates at the zero field transition \( ^{11} \). At very high fields, the energy eigenstates approximate the \( I_z^2, S_z^2 \) eigenstates. In the region of moderate fields, there is a change-over from total spin eigenstates to these high-field states, and it is in this change-over region that we find that the energy difference \( E_2 - E_1 \) has a minimum value.
The value of \( E_2 - E_1 \) is

\[
\Delta E = \frac{a}{2} - \frac{1}{\hbar} \left( m_e - m_p \right) + \sqrt{\frac{a^2}{4} + \frac{1}{\hbar^2} \left( m_e + m_p \right)^2}
\] (2.9)

which has a minimum value for

\[
H_0 = \frac{a}{4 \sqrt{m_e m_p}} \frac{m_e - m_p}{m_e + m_p}
\] (2.10)

at which point the value of the energy difference is

\[
\Delta E_{\text{min}} = \frac{a}{2} \left( 1 + 2 \eta^2 / (1 + \eta) \right), \quad \eta = m_p / m_e
\] (2.11)

The value of \( a/h \) is 1 420 405 751.768(2) Hz\(^{11}\), and of \( \eta \) is 1.519 270 335(15) \( \times 10^{-3} \) for an electron and proton in a hydrogen atom\(^{12}\). Together these known values give an energy difference in frequency units of

\[
\frac{\Delta E_{\text{min}}}{\hbar} = f_0 = 765 483 207.7(3) \text{ Hz}
\] (2.12)

at \( H_0 = 6481 \) Gauss. Because of the accuracy to which \( f_0 \) is known, the magnetic resonance signal is a rather sensitive probe of the interactions of the atoms with their environment (see Chapter VI, Section 4).

2.2 Magnetic Field Homogeneity Requirements.

There are two advantages to observing the resonance at a turning point. First, a minimum frequency can be determined by measurements made around the minimum, thereby removing the requirement for high absolute accuracy in the knowledge of the magnetic field. Thus while the magnetic field might be measured with an accuracy of only one part in \( 10^6 \), the value obtained
for \( f_0 \) would be limited in accuracy only by the accuracy of the frequency measurements at fields around \( H_0 \). Second, and more important, is the fact that at \( H_0 \) the derivative of the resonance frequency with respect to magnetic field is zero, and hence to first order inhomogeneities in the magnetic field do not broaden the resonance line.

The actual degree of broadening of the transition due to inhomogeneity can be estimated from a Taylor's expansion about \( H_0 \). For inhomogeneities of the order of 1 Gauss in the sample region, which is typical for our magnet, only the second term in the expansion is appreciable. If we let \( \Delta H \) be the difference between the applied field and \( H_0 \), and \( \delta H \) be the magnitude of the inhomogeneity of the field in the sample region, we obtain a broadening \( \delta f \) equal to:

\[
\delta f = (1.31 H_0 \text{ Gauss}^{-2}) \left( 2 \Delta H \delta H + (\delta H)^2 \right)
\]

Thus in the typical measurement range of about 10 Gauss to either side of \( H_0 \), the maximum broadening will be about 25 Hz, and at \( H_0 \) it will be 1.3 Hz. This is very small relative to the measurement accuracy of the magnetic resonance frequency, which was \( \pm 30 \) Hz at best.
2.3 The Technique of Pulsed Magnetic Resonance

Pulsed magnetic resonance is widely used, and many good treatments of this technique are available for the case of a spin 1/2 particle. In this chapter, the relevant results for the spin 1/2 system are summarized in a notation which is applicable to any two state system. It is then argued that to a good approximation we can treat the hydrogen atom in our experiment as a two state system, where it is the two lowest hyperfine states which are of interest. The results for a two state system are then applied to this hyperfine transition.

In the two state system, we label the states $|1\rangle$, and $|2\rangle$ such that

$$
\begin{bmatrix}
|a| \\
|b|
\end{bmatrix} = a|1\rangle + b|2\rangle
$$

(2.14)

We define the vector operator $\hat{\mathbf{s}}$, whose matrix representation is $\hat{\mathbf{s}} = \frac{\mathbf{s}}{2}$, where $\sigma_x$, $\sigma_y$, and $\sigma_z$ are the Pauli spin matrices. The Hamiltonian can be expressed in the form

$$
\mathbf{H} = \mathbf{h_0}/2 + \mathbf{\hat{h}} \cdot \hat{\mathbf{s}}
$$

(2.15)

where $h_0$ and $\mathbf{\hat{h}}$ may be time dependent.

Let $\mathbf{\hat{J}}$ be the thermal average of the expectation value of $\hat{\mathbf{s}}$, for a system of identical, non-interacting particles of the type being discussed. By the definition of the density matrix, $\rho$, we have that

$$
\mathbf{\hat{J}} = \text{Tr} \rho \hat{\mathbf{s}}
$$

(2.16)
which implies that

\[ \rho = 1/2 + 2 \hat{J} \cdot \hat{S} = \begin{pmatrix} 1/2 + \hat{S}_z & \hat{S}_x - i \hat{S}_y \\ \hat{S}_x + i \hat{S}_y & 1/2 - \hat{S}_z \end{pmatrix} \]  

(2.17)

Since

\[ i\hbar \hat{\rho} = [\mathcal{H}, \rho] \]  

(2.18)
equations (2.15, 2.17) give

\[ \hat{J} = \frac{\hat{J} \times \hat{h}}{\hbar} \]  

(2.19)

In a pulsed magnetic resonance experiment, the Hamiltonian consists of two parts - a constant term of the form \( U_0 \hat{S}_z \) and a time dependent term of the form

\[ U_1(t)(\cos(\omega t) \hat{S}_x + \sin(\omega t) \hat{S}_y) \]  

(2.20)

\( U_1(t) \) is zero for \( t < 0 \), a constant \( U_1 \) for \( 0 < t < \tau \), and zero for \( t > \tau \).

For \( t < 0 \), the system is in thermal equilibrium, and hence all observables are constant. From elementary statistical theory \( \rho \) is given by

\[ \rho = e^{-\beta \mathcal{H}} / \text{Tr} e^{-\beta \mathcal{H}} , \quad \beta = 1/kT \]  

(2.21)

The Hamiltonian is diagonal in this representation for \( t < 0 \), and we obtain

\[ \rho = \begin{pmatrix} R & 0 \\ 0 & P_z \end{pmatrix} \]  

(2.22)
where $P_1$ and $P_2$, the populations of states 1 and 2 are given by

$$\frac{P_1}{P_2} = \exp(-\beta(E_1-E_2)) = \exp\left(\frac{-U_0}{K}\right)$$

and $P_1 + P_2 = 1$ (2.23)

From equation (2.16), we see that

$$J_z = \frac{(P_1 - P_2)}{2}, \quad J_x = 0, \quad J_y = 0$$

(2.24)

The solution to (2.19) for $0 < t < T$ is generally obtained by transforming to a coordinate frame rotating with angular frequency $\omega$ about the $z$ axis. The solution in the laboratory frame is

$$\vec{J}(t) = R[\omega \hat{k}]R[(\omega_0 - \omega)tk + \omega_1 \tau] J_z(0)$$

(2.25)

where $R$ is the rotation matrix, such that $R(\hat{k})$ causes a rotation of angle $|\hat{k}|$ about the axis $\hat{r}/|\hat{r}|$, $\omega_0 = U_0/k$, and $\dot{\omega}_1 = U_1/k$. When $|\omega_0 - \omega| \gg \omega_1$, $\vec{J}(t)$ never deviates far from the direction $\hat{k}$, (the maximum angular deviation being $\Theta_{\text{max}} \approx 2\omega/|\omega_0 - \omega|$). Since in practise $U_1$ is generally much smaller than $U_0$, $\omega_1 \ll \omega_0$, and thus the fractional difference between $\omega$ and $\omega_0$ must be very small in order to cause any substantial transverse component of $\vec{J}$. From the form of the density matrix (2.17), we see that it is also essentially unchanged when $|\omega_0 - \omega| \gg \omega_1$. In practise, $\omega$ is chosen to be
very close to $\omega_0$, such that $|\omega_0 - \omega| \ll \omega_1$, and (2.25) then becomes

$$
\begin{align*}
\dot{S}_z(t) &= S_z(0) \cos(\omega t) \\
\dot{S}_x(t) &= S_z(0) \sin(\omega t) \sin(\omega_1 t) \\
\dot{S}_y(t) &= -S_z(0) \sin(\omega t) \cos(\omega_1 t)
\end{align*}
$$

If $\tau = \tau_{\pi/2}$, where

$$
\tau_{\pi/2} \omega_1 = \pi/2
$$

then at $t = \tau_{\pi/2}$, we have:

$$
\begin{align*}
S_z(\tau_{\pi/2}) &= 0 \\
S_x(\tau_{\pi/2}) &= S_z(0) \sin(\omega_0 \tau_{\pi/2}) \\
S_y(\tau_{\pi/2}) &= -S_z(0) \cos(\omega_0 \tau_{\pi/2})
\end{align*}
$$

For $t > \tau_{\pi/2}$, (i.e. with the time dependent part of the Hamiltonian "turned off"), the solution to (2.19) is clearly

$$
\begin{align*}
\dot{S}_z(t) &= 0 \\
\dot{S}_x(t) &= S_z(0) \sin(\omega_0 t) \\
\dot{S}_y(t) &= S_z(0) \cos(\omega_0 t)
\end{align*}
$$

Since the density matrix for this system is completely determined by $\hat{S}$, the time dependence of the expectation value for any operator can be determined from the above results.

All of these results are exact and applicable to any 2-state system. The system usually treated in text books is an ensemble of non-interacting spin-1/2 particles, with magnetic moment $\mu$, in a D.C. magnetic field $H_0$ in the
direction $\hat{k}$. For $0 < t < T_{\tau}/2$, a time dependent magnetic field, $H_{1}(t)$, is applied:

$$H_{1}(t) = H_{1} \left( \hat{\imath} \cos(\omega t) + \hat{j} \sin(\omega t) \right)$$  \hspace{1cm} (2.30)

The Hamiltonian for this system is

$$\mathcal{H} = -2\mu \hat{I} \cdot \hat{H}$$  \hspace{1cm} (2.31)

and it is easily verified that in the above notation,

$$\vec{J} = \vec{M}/2\mu$$

$$U_0 = 2\mu H_0$$

$$U_1 = 2\mu H_1$$  \hspace{1cm} (2.32)

$$\omega_0 = 2\mu H_0/\hbar$$

$$\omega_1 = 2\mu H_1/\hbar$$

Before applying the above results to the lowest hydrogen hyperfine transition, we must consider three differences between the above treatment and our experimental conditions.

A) Relaxation.

The system will return to equilibrium eventually, as a result of interactions not contained in $\mathcal{H}$. The effects of these interactions are often accurately described by a modification of (2.19):

$$\dot{\vec{J}} = \frac{\vec{J} \times \hat{h}}{\hbar} - \frac{\vec{J} \times \vec{J} + \vec{J}^2}{T_2} - \frac{\vec{J} - \vec{J}(\hat{\omega})}{T_1} \hat{k}$$  \hspace{1cm} (2.33)

where $\vec{J}(\hat{\omega})$ is given by (2.24).
Equations (2.33) are called the Bloch equations. The effect of the additional terms is to make the transverse magnitude of $\mathbf{J}$ decay exponentially to zero with characteristic time $T_2$, and to return $J_z$ to its equilibrium value $J_z(0)$ with characteristic time $T_1$. Experimentally, $U_1$ can be made large enough to ensure that $\tau_{m2} \ll T_1, T_2$, and as a result equations (2.26) are still valid. Equations (2.29) become

$$\begin{align*}
\mathbf{S}_x(t) &= (1 - \exp(-t/T_1)) \mathbf{S}_x(0) \\
\mathbf{S}_y(t) &= \exp(-t/T_2) \mathbf{S}_y(0) \exp(-i\omega t) \\
\mathbf{S}_z(t) &= -\exp(-t/T_2) \mathbf{S}_z(0) \exp(i\omega t)
\end{align*}$$

(2.34)

The effect of some types of interactions is to cause a frequency shift for the precession of $\mathbf{J}$, as well as a decay; this is described by allowing $T_2$ to have an imaginary component, i.e.

$$\sqrt{T_2} \rightarrow 1/T_2 + i\Delta\omega$$

(2.35)

(B) The Counter-Rotating Field.

In this, (and most), experiments, it is most convenient to apply a time dependent Hamiltonian of the form

$$U_1 \exp(t) = U_1 \exp \cos(\omega t) S_x$$

or equivalently

$$U_1 \exp(t) = U_1 (\cos(\omega t) S_x + \sin(\omega t) S_y) + U_1 (\cos(-\omega t) S_x + \sin(-\omega t) S_y)$$

(2.37)

where $U_1 = U_1 \exp/2$

The first term is of the same form as (2.20) while the second term has negligible effect, since its frequency differs by about $2\omega_0$ from $\omega_0$. (As discussed earlier, a time dependent component this far off resonance will cause an angular deviation in $\mathbf{J}$ of $\theta \leq \omega_1/|\omega_0 - \omega| \approx \omega_1/2\omega_0$.) Thus the effect of the time
The dependent Hamiltonian in (2.36) is the same as that in (2.20), where \( U_1 = \frac{U_1 \text{exp}}{2} \).

(C) Other States

In many magnetic resonance experiments, the system in question has more than two possible states, yet it is a valid approximation to treat it as though the only states are the two which differ by energy \( \hbar \omega_0 \), since the effect of the time dependent part of the Hamiltonian on the elements of the density matrix outside the manifold of these two states is very small. This is a result of the fact that the frequency of the time dependent part of the Hamiltonian must be very close to the resonance frequency in order to significantly change the density matrix elements for a pair of states. As long as the energy differences between all other pairs of states are significantly different from \( \hbar \omega_0 \), the time dependent Hamiltonian will be far off resonance and hence by analogy will not change the density matrix elements corresponding to these pairs of states. For the purposes of this magnetic resonance experiment, then, it is permissible to treat the hydrogen atom as a two state system with energy eigenstates (1) and (2) shown in Fig. (2.1).

The transition between these two states is observed by applying an oscillating magnetic field in the \( \hat{z} \) direction:

\[
\hat{H}_\text{exp}(t) = \hat{c} H\text{exp} \cos(\omega t)
\]  

(2.38)

and observing the voltage induced in a resonator by the
oscillating x component of the ensemble magnetization.

The time dependent Hamiltonian is

$$H_{R.F.} = -m_x H_1 \exp$$

(2.39)

where \(m_x\), the x component of the magnetic moment operator is,

$$m_x = 2 \mu_p I_x - 2 \mu_e S_x$$

(2.40)

The matrix elements of \(m_x\) are easily evaluated:

$$m_x = \begin{pmatrix}
0 & \cos(\theta) \mu_p + \sin(\theta) \mu_e \\
\cos(\theta) \mu_p + \sin(\theta) \mu_e & 0
\end{pmatrix}
\begin{pmatrix}
|1\rangle \\
|2\rangle
\end{pmatrix}$$

(2.41)

Thus

$$m_x = 2 \left( \cos(\theta) \mu_p + \sin(\theta) \mu_e \right) S_x$$

(2.42)

and the time dependent Hamiltonian (2.39) gives a value for \(U_1 \exp\) in (2.36) of

$$U_1 \exp = 2 \left( \cos(\theta) \mu_p + \sin(\theta) \mu_e \right) H_1 \exp$$

(2.43)

and therefore

$$U_1 = \left( \cos(\theta) \mu_p + \sin(\theta) \mu_e \right) H_1 \exp$$

(2.44)

\(\tau_{\pi/2}\) is given by (2.27):

$$\tau_{\pi/2} = \frac{\hbar \tau_{\pi/2}}{U_1} = \hbar \frac{\tau_{\pi/2}}{2} \left( \left( \cos(\theta) \mu_p + \sin(\theta) \mu_e \right) H_1 \exp \right)^{-1}$$

(2.45)

The ensemble average of \(m_x\) is

$$\langle m_x \rangle = 2 \left( \cos(\theta) \mu_p + \sin(\theta) \mu_e \right) \langle S_x \rangle = 2 \left( \cos(\theta) \mu_p + \sin(\theta) \mu_e \right) S_x$$

(2.46)

Thus after the \(\pi/2\) pulse, \(\langle m_x \rangle\) oscillates with frequency \(\omega_0\),

and initial amplitude

$$A(\frac{\tau_{\pi/2}}{2}) = 2 \left( \cos(\theta) \mu_p + \sin(\theta) \mu_e \right) S_x(0)$$

(2.47)
where

\[ J_z(0) = (P_1 - P_2)/2 \]  \hspace{1cm} (2.48)

These results are the same as one would obtain for spin 1/2 particles with magnetic moment

\[ \mu_{\text{eff}} = \cos(\theta)\mu_p + \sin(\theta)\mu_e \]  \hspace{1cm} (2.49)

The value of \( \mu_{\text{eff}} \) is \( 3.76 \times 10^{-22} \) erg/Gauss or 26.6 \( \mu_p \).
CHAPTER III  THE PRODUCTION OF ATOMIC HYDROGEN GAS

In this experiment, atomic hydrogen gas was produced by dissociating $H_2$ molecules in an R.F. discharge. The important design characteristics for the discharge assembly are:

1) R.F. frequency, power, and coupling
2) Discharge gas pressure
3) Gas flow rate
4) Type of wall surface

These will be discussed sequentially.

In an R.F. discharge, the electrodes are outside the discharge tube, and the frequency must therefore be high enough that charge does not build up on the walls of the discharge tube during the R.F. cycle and thus screen out the electric field. We chose to operate at 145 MHz because we had a narrowband commercial power amplifier in this range; this frequency was found to be suitable. In order to dissociate the $H_2$ molecules at the typical rate of $7.5 \times 10^{18}$ sec$^{-1}$, the dissociation energy for $H_2$ of 4.5 eV leads to a required power input of about 2 watts. Of course there are many other forms of power dissipation in the discharge, and so it is advisable to have an R.F. power input considerably greater than this. By feeding the 4Watt 145 MHz output of a homemade oscillator-amplifier into the power amplifier, we obtained a maximum output of 75 Watts. This R.F. power was coupled to the discharge assembly via a matching network consisting of two variable length tuning stubs separated by a 1/4 wave length of the transmission line used. A Bird Model 43 directional power
meter was employed in the transmission line to measure the amount of transmitted and reflected power.

Fig. 3.1 shows the discharge tube and R.F. electrode assembly used in this experiment. The electrodes, A, together with the 8-turn, 1.5 cm diameter coil, B, formed a tank circuit with resonant frequency 145 MHz to match the R.F. power source. The transmission line coupled to the tank circuit by means of two turns of wire, C, in Fig. 3.1, wound on the 8-turn discharge coil. R.F. shielding was accomplished by housing the discharge assembly in a copper box large enough to avoid detuning the resonator. (About 6" X 6" X 6".) Cooling of the discharge tube was accomplished by blowing compressed air over it.

It was found that the discharge would operate over a range of H₂ pressures from as low as a few milliTorr to about one Torr. Under most conditions, however, the discharge required some effort to start. One method involved adjustment of the tuning network to optimize the R.F. coupling when the discharge was in the "off" state, thus producing very high voltages in the discharge resonator circuit. After the discharge started, the network was re-tuned to optimize coupling under operating condition. Another method which worked as well was to start the discharge with a Tesla coil.

The greatest numbers of atoms were generally detected in the cryostat when the visible light emitted from the discharge was predominantly that of the Hα emission line. This coincided with maximization of the R.F. power dissipated in the discharge. Under these conditions the color of the discharge was an
Figure 3.1 Hydrogen R.F. discharge assembly (3/4 full scale)
extremely bright, deep red. Thus a good measure of the quality of the discharge was the radiant light intensity as measured by a cadmium sulfide photo-resistor placed in the copper box near the discharge tube. (This device weights the red portion of the visible spectrum more heavily than does the human eye.) This "quality" measurement was useful for the purpose of optimizing the R.F. coupling, and finding the most suitable gas pressure, which was generally in the range of 50-300 milliTorr of H₂.

The typical H₂ flow rate chosen was about 7.5 \times 10^{18} \text{ sec}^{-1}, as this would deposit 1 cm³ of solid hydrogen in the cryostat per hour of operation, which was deemed to be the maximum safe rate. The only practical way to limit the flow under these conditions was by choosing the correct diameter for the exit hole, D in Fig. 3.1, of the discharge tube. The formula for the exit rate of gas from a hole whose diameter is smaller than the mean free path in the gas is

\[ R = A n \sqrt{kT/2\pi m} \]  

(3.1)

where A is the area of the hole, and n is the gas density. With a flow rate of 7.5 \times 10^{18} \text{ sec}^{-1} and typical density of 2 \times 10^{16} \text{ cm}^{-3}, (3.1) implies a diameter for the exit hole of 1.0 mm. Since the mean free path is of order 1 mm at this density, this result was expected to be roughly correct, as was found to be the case.

From simple diffusion theory, one can estimate the mean rate at which a given hydrogen atom in the discharge will contact the tube wall. At .3 Torr, in a tube of this size,
this rate is of order $5 \times 10^3\text{ sec}^{-1}$. At a flow rate of $7.5 \times 10^{18}\text{ sec}^{-1}$, a discharge volume of $5\text{ cm}^3$, and $0.3\text{ Torr}$ pressure, the mean residency time for an atom in the flow tube is $10\text{ msec}$, and thus it is expected that an atom will contact the tube wall about 50 times before leaving the discharge. Clearly, then, it is desirable to choose a wall material which does not strongly catalyze the recombination of $H$ into $H_2$. (It has long been known that metal electrodes are particularly bad in this respect - this is the main reason for employing an R.F. discharge with external electrodes).

We used a pyrex discharge tube, and cleaned the inner surface as follows: It was first washed with soap and water, tricloroethylene, acetone, and then water. The tube was then filled with chromic acid, drained, and rinsed with distilled water. Although this procedure resulted in good quality discharges, this quality would deteriorate with time, presumably because of impurities in the gas entering the discharge or because of degradation of the glass surface by the chemical action of the discharge. This problem was solved with the well-known technique of coating the discharge tube with polyphosphoric acid - a very viscous liquid which remains as a film on the surface of glass and which has a very low vapour pressure (less than a few milliTorr after about a day of pumping.) Although we do not understand why the acid improves the discharge, it works so well that we found it advisable to use it.

In order to minimize recombination in the pyrex flow tube leading from the discharge to the detection region, the interior
of the tube was teflon coated. The tube was first cleaned
in the same manner as the discharge tube, and then coated
with duPont FEP Code 120 teflon dispersion diluted with an
equal quantity of distilled water. After the film was
dried with a slow flow of helium, it was heated in an oven
to 390°C under a flow of oxygen, and then cooled slowly
(less than 1°C per minute) to below 200°C. At this point the
oven was turned off and allowed to cool to room temperature.\textsuperscript{14}

The connection of the discharge tube to the gas handling
system is discussed in Section 5.2.
CHAPTER IV THE 765 MHz PULSE SPECTROMETER

4.1 Block Diagram of the Spectrometer

As was discussed in Section 2.3, the electronic system needs first to provide short pulses of R.F. power at the resonance frequency, with the correct product of intensity and time to produce a \( \pi/2 \) pulse. In addition, immediately after the pulse is sent down the transmission line, the system must be able to receive and amplify the extremely weak free induction decay, (typically \( 5 \times 10^{-15} \) watts) arriving along the same transmission line. Next, the system must process the received signal in order to make it useful to the experimenter, by translating it to a low frequency. Finally, adequate signal to noise ratios require averaging of many free induction decays.

Since typical free induction decays we observed lasted a time in the range of \( 10-1,000 \mu \text{sec} \), a reasonable choice for the pulse duration was a few \( \mu \text{sec} \), which required pulse power levels of tens of milliwatts, some \( 10^{13} \) greater than the typical signal strength. Yet the amplifier system which measures this very weak signal must be able to recover from the saturation caused by this huge pulse in a time of a few \( \mu \text{sec} \), and at the same time have an input noise level as low as possible.

The pulse spectrometer system which we employed, and which satisfied these requirements admirably, was designed by Walter N. Hardy. In the description of the design of this system which follows, the manufacturer and model of each piece of equipment will be given, and where the piece is "homemade", reference will be given to a publication describing its design.
A block diagram of the spectrometer is given in Fig. 4.1. The diagram has been divided into four sections. The top most section produces the pulses of R.F. power at the resonant frequency, and sends them to the diplexer (the next section down.) In addition, it sends a continuous R.F. signal which is coherent with the pulses to the signal processor (bottom section), for use as a reference. The diplexer acts as an electronic relay. In the "on" state, it feeds the R.F. pulse from the pulse generator to the resonator in the experimental apparatus, and in the "off" state it connects the output from the resonator (i.e. the free induction decay and the noise) to the amplifier (third section down). The amplifier section amplifies the signal to the level of millivolts, and feeds it to the signal processor, which mixes it with the reference signal from the R.F. pulse generator to transform it down to a moderately low frequency (∼100 kHz), and then signal averages and presents the output on an x-y recorder. The duration and repetition rate of the R.F. pulse is controlled by the duration and repetition rate of the D.C. pulse from the pulse generator. The pulse generator also triggers the diplexer, so that it is "on" when the R.F. pulse arrives, as well as the sweep on a monitoring oscilloscope and the signal averager. The details of these sections will now be discussed.

The R.F. signal used to produce the R.F. pulses was generated by an HP 8640A signal generator, used with an output of about 100 mW. The frequency of this generator was divided by 10 and phase locked to the Schomandl STO 100M
Figure 4.1  765 MHz. pulse spectrometer.
frequency synthesizer. The divide-by-ten operation was achieved by modifying the HP 5327A frequency counter so that the output of its prescaler was available at the back of the instrument. The counter sampled a portion of the power from the R.F. generator via a 10db directional coupler and displayed the frequency for reference purposes. In addition, the divided-by-ten signal became the local oscillator input of a mixer, so as to produce a beat frequency with the signal from the synthesizer. This difference frequency output of the mixer was then connected to the F.M. input of the R.F. generator, thus completing the phase-lock loop. This somewhat elaborate arrangement was required to hold the frequency drift of the R.F. generator to a level much less than the resolution of the line centre, which for good signals was as small as 30 Hz.

As will be discussed shortly, this signal generation system was set to produce a frequency of approximately one-half the resonance frequency, and was doubled in later stages. In order to obtain a reference signal at the resonance frequency, for use in the signal processing section, a 10db reduced signal was taken from a second directional coupler, and fed through a doubler to the signal processing section.

It is convenient at this point to discuss two aspects of the signal generator frequency, the first being that we operate at half the resonant frequency and double at the final power stage. Initially this method was chosen because our R.F. generator could not produce a 765 MHz signal. However, the method also offered a distinct advantage - the extremely large on-off ratio for the r.f. pulses is more easily accomplished
when the pulse is produced by doubling another signal, since the doubling was performed by a component driven into nonlinear operation - a condition which can be rapidly started and stopped with a D.C. control pulse. The second aspect of the R.F. frequency warranting discussion is that it was set to produce a doubled signal off resonance by an amount \( \Delta f \), so that the reference to the signal processing section would yield a beat frequency \( \Delta f \) upon mixing with the free induction signal. \( \Delta f \), (usually between 10 and 50 kHz.), was chosen so that between 5 and 20 beats would occur in \( T_2 \), in order to allow measurement of the envelope of the decay while minimizing the noise bandwidth. As discussed in Section 2.3, the angular frequency offset, \( 2\pi \Delta f \), must be small compared to \( \omega_1 = \pi/2(\tau_T/2)^{-1} \), in order to have a \( \pi / 2 \) pulse. This was always the case.

The R.F. signal was attenuated 20db and fed into a mixer which acts as a switch which is "closed" by a pulse from the pulse generator. The purpose of starting with a large signal from the R.F. generator and then attenuating it before using it for counting, reference, and pulse production is to make these operations as independent of one another as is reasonably possible.

The signal leaving the mixer-switch, (in the form of R.F. pulses at half the resonance frequency), was fed into one half of an HP 8447F amplifier, through an isolator, and into the homemade doubler-amplifier. The isolator further decreased the possibility of the pulse-production system interacting with the signal generator, and hence affecting the continuous
reference signal fed to the signal processing section. The doubler amplifier is also switched into operation only when the half-frequency R.F. pulse reaches its input; this switching is produced by a D.C. pulse from the pulse generator. The 765 MHz output was then attenuated to the correct level for a \( \pi/2 \) pulse, and was fed to the diplexer.

The purpose of the diplexer, (a homemade unit)\(^{16}\), is to electronically connect the output of the R.F. pulse generation section to the transmission line leading to the resonator in the experimental apparatus, during the R.F. pulse only. At the same time, the diplexer provides high attenuation between the transmission line and signal amplifier section, so as to minimize the saturation from the R.F. pulse. In the interval between pulses, the diplexer does the reverse - the amplifier section is connected directly to the transmission line and is isolated from the pulse generation section. This action is controlled by a D.C. pulse from the pulse generator which changes the impedance of PIN diodes at key points in a coaxial resonator system, as described in reference (16). A 20db directional coupler was connected between the diplexer and the transmission line leading to the resonator, and each output was passed through a 10db attenuator and into a diode detector. Thus one detector measured the intensity of the incident R.F. pulses (as a check on the functioning of the pulse generation system and diplexer), and the other the intensity of the reflected pulse leaving the resonator, (which should be zero when the resonator is critically coupled to the transmission line.)
The amplifier chain receiving the signal from the resonator via the diplexer consisted of a broadband Avantek UTO-1011 amplifier, feeding into a homemade, narrowband (765 MHz) amplifier\textsuperscript{17}, which passed through a high pass filter to remove some low frequency transients produced by the diplexer, and finally into the other half of the HP 8447F amplifier. The output from this amplifier was fed to the mixer in the signal processing section.

In this mixer, the free induction signal beat with the slightly different frequency reference signal from the pulse generation section so as to produce an output signal of magnitude proportional to that of the free induction signal and of frequency equal to the difference between the free induction and reference frequencies. This signal, which was almost always smaller than the noise, was monitored and amplified by a Tetronix 541A oscilloscope, triggered by the pulse generator. While the signal could not always be seen on the oscilloscope, the display was useful as a monitor of the over-all system functioning (such as the "appearance" of the noise, the amplifier recovery time after the pulse, etc.). The frequency-translated free induction signal, after amplification by the oscilloscope, was fed to the Nicolet 1174 signal averager. This device would store the voltage level obtained by sampling the signal at 1,024 points in time after each pulse, with the interval between points as small as one microsecond. The result of this sample would be displayed on a cathode ray tube, and the results of sampling after successive pulses would be added to the previous measurements, so...
that the displayed signal would grow in proportion to the number of pulse intervals sampled. Since the noise is random, however, its r.m.s. magnitude grows in proportion to the square root of the number of measurements. Thus the net signal to noise ratio for the signal averager display would increase in proportion to the square root of the number of measurements. Since the pulse repetition rate was as high as 1 kHz, this was a very convenient and usually essential method of improving the net signal quality. (It was not unusual to signal average for as many as 262,000 pulses which would take about five minutes.) A paper copy of the CRT display was obtained using an x-y recorder.
4.2 Characteristics of the Spectrometer

Before using the completed spectrometer for making quantitative measurements, four features of the system had to be determined.

The first was the noise temperature, which is defined to be the temperature of a 50Ω resistor which when connected to the input of the system will double the observed noise power. This was measured by connecting an Aerospace NS-LB noise generator to the input and adjusting it to increase the r.m.s. amplitude of the noise output by $\sqrt{2}$. The noise temperature obtained was 170K.

The next feature checked was the recovery time of the system - that is the time taken after the R.F. pulse for the system to recover full sensitivity. This time was readily observable on the oscilloscope as a region of wild fluctuations devoid of high frequency noise. The noise took on a completely normal appearance, indicative of recovery, 3-10 μsec after each pulse.

The third check involved the frequency accuracy of the frequency synthesizer, R.F. generator, and counter system. This frequency was stable to within our frequency counter resolution of 1 Hz. The absolute accuracy of the counter was checked by using it to measure the frequency of the color sub-carrier pulse used in an American network television broadcast. This signal is tied to an atomic clock and is monitored by the U.S. National Bureau of Standards. This check established the counter error to be less than 10 Hz.
The fourth, and by far the most difficult check on the system was the calibration of its sensitivity. This was accomplished as follows. A continuous signal at the resonance frequency was obtained from the -10dB output of the directional coupler prior to the mixer. (The directional coupler was always in place, so that obtaining the signal would in no way alter the characteristics of the system.) This signal was then translated to a frequency differing by 10 kHz, by means of a single-side-band generator, which mixed the incoming signal with a 10 kHz signal so as to produce only the two sidebands, and then selectively canceled one of them. Upon feeding the sideband signal to the diplexer input, the spectrometer output would be a 10 kHz beat, which could be coherently added by triggering the signal averager with the original 10 kHz signal in the single-side-band generator. By attenuating the signal applied to the diplexer to a known magnitude (comparable to that of the free induction decay), it was possible to perform a calibration of the system as a whole. The chief uncertainty in this procedure resulted from the uncertainty in the attenuators used, which were calibrated with a General Microwave 460B power meter. With this calibration, the absolute power of the free induction signal could then be inferred from the spectrometer output.
4.3 Resonator Design

At a frequency of 765 MHz, conflicting demands are placed on the resonator to be employed in detecting the atoms. A circuit composed of ordinary coils and capacitors is inappropriate because of the high inductive impedance of wires at these frequencies, which makes it difficult to have a uniform magnetic field confined mainly to the sample region. Moreover, because of the concentrated surface currents in such a design, the ohmic losses are quite high and the $Q$ of the circuit is therefore quite low. An alternative which overcomes these problems at high frequencies is the use of a resonant cavity. Unfortunately, a 765 MHz resonant cavity has a minimum size of order 20cm - far too large to be convenient in a cryogenic apparatus.

The somewhat novel resonator design we chose, (see Fig. 4.2), overcomes both of these problems. In essence, the resonator consists of a single turn coil in parallel with a parallel plate capacitor. The resonator was machined out of a single block of copper in order to avoid differential thermal contraction. The capacitor gap was cut with a thin saw blade and then reduced to zero thickness by compression of the copper in a hydraulic press. The gap was then opened out to the required size for a resonance of 765 MHz by means of a copper tuning screw which was prevented from "shorting out" the capacitor gap by means of a thin piece of mylar. (See Fig. 4.2).

With this design, the $Q$, (the ratio of the resonant frequency to the full width at half maximum), was greater
Figure 4.2 765 MHz resonator, tuning rod and coupling loop.
(scale 1:2)
than 1,000, and it was possible to tune the resonant frequency from 200-900 MHz by adjusting the copper screw. Fine tuning was obtained using a tuning loop consisting of a copper ring of about the same diameter as the resonator bore. The ring was mounted coaxially with the resonator and could be moved from within a millimeter of the resonator to about 15 mm away by means of a moveable dielectric support rod, as shown in Fig. 4.2. In effect, the loop acts to decrease the inductance of the single turn coil by opposing any change in magnetic flux through its interior, in much the same way as the effective inductance of the primary winding of a transformer can be reduced by shorting the secondary. This method allowed remote tuning over a range of about 20 MHz, which was satisfactory for the purpose of overcoming the frequency shift which occurs on cooling to cryogenic temperatures. (This shift was always less than 2 MHz.) This tuning method would slightly affect the Q; this change in Q was always less than 20%.

Coupling the resonator to the 50Ω coaxial transmission line leading from the 765 MHz spectrometer was accomplished by mounting a single turn loop as a termination to the transmission line, so that it was coaxial with the resonator, and on the opposite side from the ring, as shown in Fig. 4.2. By adjusting the distance between the loop and the resonator, (several mm), it was possible to obtain critical coupling with the transmission line. There were thus two remote position adjustments to be made to tune the resonator to match the 765 MHz spectrometer - frequency adjustment and coupling adjustment. While these were not 100% independent, it was
nevertheless very easy to quickly obtain critical coupling.

Although an analytic solution to the fields in the resonator has not, and probably cannot be found, a simple approximation to them serves to demonstrate the basic behavior of the resonator, and allows a reasonably accurate theoretical calculation of the $Q$. The approximation consists of ignoring edge effects. First, the resonator is assumed to be infinitely long, such that spreading of the fields at both ends is not considered. Second, the fringing fields of the capacitor gap are ignored, which is a reasonable assumption because the gap is very narrow relative to the size of the plates. Under these conditions the magnetic field in the bore of the resonator will be uniform and in the axial direction as in a perfect solenoid.

Moreover, the electric field in the capacitor gap will be uniform and perpendicular to the plates as in a perfect parallel plate capacitor, and will oscillate $90^\circ$ out of phase with respect to the bore magnetic field. Since this uniform changing electric field requires a uniform curl in the magnetic field in the same direction, and since the magnetic field outside the resonator will be close to zero, the magnetic field in the capacitor gap must be in the axial direction, and must decrease linearly from the value it has in the bore at the innermost point in the gap, to zero at the outermost point in the gap. (Actually, when the resonator is of finite length and within a metal enclosure as in our apparatus (see Fig. 5.1), the magnetic field outside the resonator will not be zero, since the magnetic field lines must form closed
loops inside the enclosure. However, since the cross section-
al area outside the resonator is at least five times that inside, the external field is smaller by that amount, and this approximation is fairly good.)

With these fields, the resonant frequency and the Q can be determined. Let \( r_0 \) be the radius of the resonator bore, \( a_0 \) be the width of the capacitor plates, and \( b \) the thickness of the capacitor gap. Let the magnetic field in the bore be

\[
H_i(t) = H_i \cos(\omega t)
\]

which implies that in the capacitor gap

\[
(\nabla \times H)_{\text{gap}} = \frac{H_i}{a_0} \cos(\omega t)
\]

Also, let the electric field in the capacitor gap be

\[
E(t) = E_0 \sin(\omega t)
\]

In order for the total electromagnetic energy to remain constant, it must be the case that

\[
\int dA \ E_0^2 = \int dA \ H_i^2 \quad \text{(c.g.s.)}
\]

which implies (for \( ab \ll 1 \)) that

\[
E_0 = \left(\frac{\pi}{ab}\right)^{1/2} H_i
\]

We can now employ the Maxwell equation

\[
\nabla \times \vec{H} = \frac{1}{c} \frac{\partial \vec{E}}{\partial t}
\]

for the fields in the capacitor gap, to obtain

\[
\frac{H_i}{a_0} \cos(\omega t) = \frac{\omega}{c} \left(\frac{\pi}{ab}\right)^{1/2} H_i \cos(\omega t)
\]
which implies

\[ \omega = \frac{c}{r_0} \left( \frac{b}{\pi a} \right)^{1/2} \tag{4.8} \]

The calculation of the Q is straightforward but a little more complex. From the theory of simple resonators, the Q is given by:

\[ Q = \omega \frac{\text{stored energy}}{\text{mean power loss}} \tag{4.9} \]

(In our case the stored energy and power loss will be determined per unit length of the arbitrarily long ideal resonator.)

The energy per unit length is

\[ U = \frac{r_0^2}{8} H_1^2 \tag{4.10} \]

The power loss per unit length is given by\(^{18}\)

\[ \overline{P} = \left( \frac{c^2}{16 \pi^3} \right) \frac{1}{2 \delta} \oint |\vec{\nabla} \times \vec{H}|^2 \, dl \tag{4.11} \]

where \( \delta = \left[ \frac{c}{\sqrt{4 \pi}} \right] \left( \frac{2}{\omega \sigma} \right)^{1/2} \)

and \( \sigma \) is the electrical conductivity of the metal. Assuming \( a \ll \), as is the case,

\[ \overline{P} = \left( \frac{c^2}{16 \pi^3} \right) \frac{1}{2 \delta} \left[ 2 \pi r_0^2 H_1^2 \right] \tag{4.12} \]

Thus, from (4.9), (4.10), and (4.12) we obtain

\[ Q = \omega \frac{U}{\overline{P}} = \frac{r_0}{\delta} \tag{4.13} \]
Substituting for \( \delta \), we have

\[
Q = \sqrt{2\pi} (\omega \sigma)^{1/2} \frac{r_0}{c} \tag{4.14}
\]

Converting to MKS units, we obtain

\[
Q = \frac{\sqrt{2}}{2} i (\mu_0 \sigma \omega)^{1/2} \tag{4.15}
\]

and substituting for \( \omega \), we have

\[
Q = \frac{\sqrt{2}}{2} \left( \frac{b}{\pi a} \right)^{1/2} (\mu_0 \sigma_0 \sigma)^{1/2} \mathrm{(M.K.S.)} \tag{4.16}
\]

Both the prediction for the resonant frequency and the \( Q \) were tested on a large model resonator of precisely known dimensions, and were found to agree well with the experimental values. In addition the magnetic field in the actual resonator used was probed with a small loop of wire and was indeed found to be reasonably uniform and in the axial direction. We are thus very confident that we understand the behavior of this resonator.

In order to set the R.F. pulse length it is necessary to know the value of \( H_1 \) produced in the resonator by a continuous input power \( P \) at critical coupling. This can be calculated from equations (4.9) and (4.10), letting \( l \) be the length of the resonator:

\[
Q = \omega \frac{\frac{L_0^2}{8} H_1^2}{P} \tag{4.18}
\]
and thus

$$H_i = \frac{2}{\nu_0} \sqrt{\frac{2PQ}{\omega l}} \quad (4.19)$$

In addition we need an expression for the power flowing out of the critically coupled resonator when it is driven by an oscillating magnetic moment $m(t) = m\sin(\omega t)$ in the axial direction. This calculation will proceed in three steps. First, the power input to the resonator from the oscillating moment, $P_{in}$, will be determined as a function of $H_i$. Second, the power loss of the resonator due to ohmic losses, $P_n$, and due to power flowing into the transmission line, $P_s$, will be determined. Finally, the fact that at steady state $P_{in} = P_n + P_s$ will be employed to obtain $P_s$ as a function of $m$.

The average value of $P_{in}$ is:

$$P_{in} = \bar{m} \cdot \bar{B} \quad (4.20)$$

where $\bar{B} = \bar{H} + 4\pi M$, or in our case $B = H_i + 4\pi M$ in the $z$ direction, where $V$ is the volume of the gas in the resonator. Thus

$$P_n = \left(\frac{d}{dt} m \sin(\omega t)\right)\left[H_i \cos(\omega t) + \frac{4\pi M}{V} \sin(\omega t)\right] = \frac{mH_i \omega}{2} \quad (4.22)$$

The value of $P_s$ can be found from (4.19), since at critical coupling the power flowing out of the resonator, when it is made to oscillate by the oscillating magnetic moment, will be the same as that which must flow down the transmission line to make it oscillate to the same extent without any oscillating magnetic moment. Thus
\[ H_1 = \frac{2}{r_0} \sqrt{\frac{2P_0}{\omega \lambda}} \]  
\[ \text{and therefore} \]
\[ P_s = \frac{H_1^2 \omega \lambda r_0^2}{8Q} \]

\( P_\Omega \) can also be obtained from (4.19), because energy conservation requires that the power flowing down the transmission line to sustain oscillations in the resonator will equal the ohmic losses at critical coupling. Thus

\[ P_\Omega = P_s = \frac{H_1^2 \omega \lambda r_0^2}{8Q} \]

Since \( P_{\text{in}} = P_\Omega + P_s = 2P_s \), we obtain from (4.22 and 4.24)

\[ \frac{mH_1}{2} = \frac{H_1^2 \omega \lambda r_0^2}{4Q} \]

Solving for \( H_1 \) and substituting into (4.24), we obtain

\[ P_s = \frac{m^2 \omega Q}{2 \lambda r_0^3} \]  
\( \text{(c.g.s.)} \)  

These results can now be combined with those of section 2.3 to determine the requirements for a \( \pi/2 \) pulse, and the expected signal strength from a typical number of hydrogen atoms. The parameters for our resonator were as follows:

\[ Q = 1180 \quad (4.2 \text{ K, unloaded } Q) \]
\[ r_0 = 6.35 \text{ mm} \]
\[ \lambda = 12.7 \text{ mm} \]
\[ \omega = 2\pi \times 765 \text{ MHz} = 4.81 \times 10^9 \text{ sec}^{-1} \]
Equation (4.19) thus becomes

\[ H_1 = \left[ 1.96 \times 10^{-3} \text{ Gauss} \ (\text{erg/sec})^{1/2} \right] P^{1/2} \tag{4.28} \]

and with a typical operating R.F. pulse power of \( P = 0.079 \) Watts, or \( 7.9 \times 10^5 \) erg/sec, we obtain \( H_1 = 1.74 \) Gauss. Using (2.45),

\[ \frac{\tau_{\pi/2}}{2} = \frac{\tau_0}{2} \left( (\cos(\theta) \omega_p + \sin(\theta) \omega_e) H_1 \right)^{-1} \]

we obtain \( \tau_{\pi/2} = 2.5 \mu \text{sec} \).

Let us now calculate the expected signal power, \( P_s \), with a typical number, \( N = 10^{14} \), of atoms in the resonator, with the spin system in equilibrium at 4.2 K. Using the above resonator parameters, (4.27) becomes

\[ P_s = \left[ 5.54 \times 10^{-12} \ (\text{erg/ sec})(\text{erg/Gauss})^{-2} \right] m^2 \tag{4.29} \]

Immediately after the \( \pi/2 \) pulse, the value of \( m \) is given by (2.47) and (2.48):

\[ m = N \left( \cos(\theta) \omega_p + \sin(\theta) \omega_e \right) (P_+ - P_-) \tag{4.33} \]

At 4.2K, the fractional populations dictated by (2.23) are

- \( P_1 = 0.27717 \)
- \( P_2 = 0.27475 \)
- \( P_3 = 0.22487 \)
- \( P_4 = 0.22320 \)

so that \( P_1 - P_2 = 0.00242 \), and the value of \( m \) in (4.33) is

\[ m = (9.1 \times 10^{-25} \text{ erg/Gauss}) N \tag{4.34} \]

With \( N = 10^{14} \), the value of \( P_s \) obtained from (4.29) is

\( 4.59 \times 10^{-8} \) erg/sec, or \( 4.59 \times 10^{-15} \) Watts.
4.4 Quantitative Analysis of Graphic Output

As mentioned in section 4.1, the output of the spectrometer system is a graph produced by an x-y recorder. The total x-axis extent of the graph corresponds to a known time interval set by the crystal clock in the signal averager, and the full scale displacement on this chart is known, via the calibration procedure, to correspond to a certain input power to the spectrometer.

Fig. 4.3 shows a typical output curve. For the purposes of this experiment, such curves contain three pieces of information - the initial signal intensity, (that is the fraction of full scale of the oscillation amplitude at the beginning of the trace), the frequency of the oscillations, and, for exponentially decaying oscillations (as was normally the case), the decay time of the oscillation magnitude.

The frequency of the graph oscillations was determined by counting the largest possible number of zero crossings of the curve, and dividing half this number (i.e. the number of cycles) by the time interval, which was obtained from the known time base of the graph. The actual frequency of the free induction decay could then be obtained by appropriate addition or subtraction of this frequency to that of the local oscillator. The largest error resulted from noise in the signal which lowered the accuracy of the time interval measured on the graph; this error could be estimated from the scatter in repeated analysis of the same signal.

The initial amplitude and decay time was determined by measuring the amplitude of the oscillation as a function of time.
Figure 4.3 A typical free induction decay.
Providing the decay is reasonably exponential, and the decrease in amplitude per oscillation is not too great, an accurate, and simple way of doing this is that illustrated in Fig. 4.3. A line is drawn between two adjacent maxima of the oscillation, and the vertical distance from the minimum between them to the line is measured and is taken to be twice the amplitude at the time at which the minimum occurred. For an approximately exponential decay, the fractional error introduced by this procedure is independent of the amplitude of the oscillations, and hence will not affect the measure of the decay time. Moreover, this fractional error in the amplitude obtained is of order $a^2$ where $a$ is the fractional decrease in amplitude per oscillation. The error thus contributed to the initial amplitude value obtained was of order 1%. The advantage of this technique is its simplicity, quickness, and insensitivity to slow background drift of the center point of the oscillation.

The data obtained for the amplitude as a function of time was then plotted on log-lin paper, as shown in Fig. 4.4, and the slope and intercept of the resulting straight line provided the decay time and initial amplitude of the oscillation.
Figure 4.4 Determination of $T_2$ and initial amplitude $A(0)$ for a free induction decay.
CHAPTER V EXPERIMENTAL DESIGN

5.1 Overall arrangement.

Fig. 5.1 shows the arrangement of the H-atom flow tube, resonator, resonator tuning rod and magnetic resonance transmission line inside the liquid helium dewar, within the pole caps of the electromagnet. The mixture of molecular and atomic hydrogen gas, after leaving the discharge tube, passes down the 1.0 meter long teflon coated 12mmOD pyrex flow tube to the detection region. This flow tube is sealed with an O-ring seal as it passes through the flange into the evacuated region of the system. The flow tube terminates inside the copper can which lies between the 12" poles of the electromagnet. A 1/2" OD stainless steel tube surrounds the flow tube between the flange and the can to maintain the vacuum seal.

The resonator itself is supported by a fiberglass support plate above the end of the flow tube, with its bore coaxial with the tube. At liquid helium temperatures, all of the H$_2$ gas would eventually freeze on the walls of the copper can, whereas at higher temperatures it was pumped out of the system with a diffusion pump connected to the copper enclosure by means of a pipe which for reasons of clarity is not shown in Fig. 5.2. (See section 2 of this chapter).

The tuning of the resonator was accomplished by holding the tuning ring in place beneath the resonator with a rod of micarta, which was attached to a 1/8" OD thinwall stainless steel tube which passed out of the copper can and through the top flange so that its vertical position could be adjusted. The vacuum seal of the system was maintained by surrounding this
Figure 5.1  Probe in dewar vessel.  (scale 1:3)
stainless steal tube with a 3/16" thin wall tube which sealed to the resonator enclosure can and to the top flange. Above the flange, the 1/8"s.s.tube passed through an O-ring seal, which served both as a vacuum seal and as a means of holding the tuning rod in a fixed position. The coupling loop was positioned above the resonator (hence around the flow tube), and was held in place by the SMA semi-rigid 50Ω coaxial transmission line which it terminated. This transmission line passed out of the copper can and through the flange with the same 3/16" tube and O-ring seal arrangement as that which vacuum-sealed the 1/8" OD tuning rod. Above the flange, the transmission line coupled to the 765 MHz pulse spectrometer system. Both the transmission line and the tuning rod had square pieces of brass attached to them which moved in brass slots in such a way as to prevent rotation of the rods, but which allowed vertical motion, so that the rotational alignment of the coupling loop and tuning ring was maintained at all times.

In the remainder of this chapter, further details of design will be presented in the following three categories - gas handling, the electromagnet system, and cryogenic techniques.

5.2 Gas Handling

The molecular hydrogen gas supplied to the discharge tube was obtained from an ultra-high purity (99.999%) high pressure gas cylinder, by means of a regulator which reduced the pressure to about 5 psi. This gas then passed through a fine metering valve, which acted as the flow control for the H₂ gas. This valve was adjusted so as to create the correct operating
pressures of about 350 mTorr in the discharge tube. The pressure was measured immediately after the metering valve by means of a 20mm Hg full scale Wallace & Tiernan gauge and also by a 200 mTorr mid-scale thermocouple gauge. (The thermocouple gauge had to be used in conjunction with a calibration table for use with H₂ gas – the reading on the gauge is approximately twice the true pressure of H₂.) It was assumed that the pressure measured by these gauges was a good measure of the pressure in the discharge tube, since the main restriction to the flow beyond the metering valve was the small hole at the outlet of the discharge tube. In the pressure range of 100mTorr to several Torr, the flow rate was roughly proportional to pressure.

The hydrogen gas was piped from the metering valve and pressure measurement assembly to the discharge tube through 1 meter of 3/8" OD Poly-flo tubing, at which point the tubing connected, via a Poly-flo fitting, to an O-ring seal sealing to the glass discharge tube. The discharge bulb itself was positioned about 15 cm above and 15 cm off-center from the flange on the dewar, in the same orientation as shown in Fig. 3.1. This positioning was chosen to facilitate access to the dewar, and at the same time minimize the path length from the discharge to the detection region. The discharge bulb was connected to the flow tube passing into the dewar by means of a 12mm OD pyrex tube which coupled to the discharge via a silicone-greased spherical ground glass joint, and connected to the main flow tube by a double O-ring sealing brass piece. This intermediate flow tube was internally coated with poly-
phosphoric acid. The total path length of tubing leading to the detection region was thus 1.3m.

The copper can surrounding the resonator was pumped by means of a 20 cm long 1/4" OD thinwall stainless steel tube connecting to an 60 cm long 3/8" OD thinwall stainless steel tube leading to a Leybold connector on the dewar flange. A 2.5 meter long 1 1/8" OD copper pumping line lead from this flange to a diffusion pumping station. When making measurements at liquid helium temperatures, this pumping line was not needed for pumping molecular hydrogen out of the system, because the H₂ would solidify at these temperatures, but it was nevertheless useful for the purpose of adding or removing helium buffer gas to the vacuum system. For this purpose a cylinder of ultra-high purity helium with a regulator and valve was connected to the pumping line near the diffusion pump. The pressure of helium gas could then be monitored with the ionization pressure gauge on the pumping station.

5.3 The Electromagnet System.

The electromagnet system used in this experiment consisted of a Varian V012-3B electromagnet used with 12" pole caps, and powered with a Varian V2100-B power supply. The magnetic field of 6,481 Gauss was measured with a home-made NMR magnetometer system. The NMR sample consisted of about .25 cm³ of a saturated CuSO₄ in water solution, subject to a modulation field of about 1 Gauss at 17 Hz, and the NMR spectrometer was a home-made Robinson oscillator operating at 27.590 MHz. The amplitude modulation was detected with a PAR model HR8 phase sensitive
detector using the magnet modulation signal as a reference and operating with a time constant of 3 seconds. The output of the phase sensitive detector, which was proportional to the derivative of the NMR absorption with respect to field, was fed with the appropriate sign to a varicap diode in the Robinson oscillator tuned circuit, such that the oscillator frequency would "lock on" to the centre of the NMR absorption line. The resultant frequency was measured with an HP model 5245J frequency counter, and using the known gyromagnetic ratio for protons in water of 42.576 MHz/kGauss, the magnetic field could be calculated.

Using this field measurement system, the inhomogeneity of the magnet in the 1 cm$^3$ detection region was found to be about 1 Gauss, and in addition the field profile of the magnet was measured. The magnet power supply was stable to better than 1 part in $10^5$ over periods of hours, although on several occasions its output shifted by about 1 part in $10^3$, and remained stable at this new value. This shift never occurred during a run, and we concluded that it had a different origin than did the usual very slow drift.

For routine monitoring of the field during the experiment, the water sample was located 6 cm from the resonator in the dewar, where the magnetic field was within 3 Gauss of the value in the resonator. The total uncertainty in the field was of the order of 3 Gauss, which was less than the uncertainty in our measurement of $H_0$. 
5.4 Cryogenic Techniques.

The stainless steel dewar vessel employed in this experiment was of basically conventional design. (See Fig.5.1) The liquid nitrogen vessel did not completely surround the liquid helium vessel, due to lack of space in the tail of the dewar. Instead, the bottom portion of the helium vessel is surrounded by a copper can which is held at about 77K by thermal contact to the liquid nitrogen above. The vacuum space between the outer jacket and the liquid nitrogen space contained about 100 cm$^3$ of molecular sieve material to maintain a hard vacuum, while the vacuum space between the liquid nitrogen and liquid helium contained about 1 Torr of air which provided thermal conductivity for cooling to 77K, and which would freeze out upon transferring liquid helium to the inner vessel. The liquid nitrogen would last for about 12 hours (the dewar was not super-insulated), and the 6 liters of liquid helium stored by the inner vessel would last about the same length of time with no additional energy input to the system.

The liquid helium level was detected by monitoring the current flow in each of three 100$\Omega$, 1/4 Watt carbon-composition resistors, which were mounted inside the dewar at the bottom, middle, and top of the "belly" of the liquid helium vessel. These resistors had a voltage of about 10 volts applied to them, as this was found to be optimal for observing the sudden drop in conductivity which these resistors undergo upon being covered in liquid helium as opposed to 4.2 K helium vapour. The principle behind this phenomenon lies in the fact that the
liquid helium is slightly more efficient at cooling the resistors than is the vapour, and that the carbon composition resistors increase resistance dramatically as their temperature drops. In our apparatus, the current through the resistors would drop very suddenly by about 30% upon immersion when transferring liquid helium into the vessel, and would return to the higher value when the liquid level dropped beneath them. One disadvantage to this technique was that the power dissipation (about 200 mWatt) was sufficiently high that continuous use of this detection system was impractical.

While taking measurements it was important to know the temperature of the gas in the detection region, particularly during measurements which were performed as the temperature of the system was rising above liquid helium temperatures. This temperature was determined by monitoring the resistance of a 100Ω Allen-Bradley carbon composition resistor which was mounted on the support which held the resonator in place. The resistance of this resistor was measured at room temperature, liquid nitrogen temperature, and liquid helium temperature, and these data were used to find the constants in the assumed relationship:

$$ T = \frac{B}{\ln(R) + k / \ln(R)} - A $$

(5.1)

This temperature sensor was found to have another use in the experiment - when operating at liquid helium temperatures with no helium buffer gas, the resistor was substantially heated by the recombination of hydrogen atoms on its surface. In fact, the recombination heating of the resistor was a far more
sensitive detection method for hydrogen atoms than was the magnetic resonance system. Using this detector, we were able to observe an interesting behaviour which occurred every time we transferred liquid helium into the system - the magnetic resonance signal, which had been visible at 77 K, would disappear upon cooling to 4.2 K, and the resistor-detector would indicate no recombination heating. After a period of about 5 minutes, however, some atoms would be detected by the resistor, and after a few more minutes the heating effect would reach its maximum value, whereupon the usual strength of magnetic-resonance signal would be observed. We concluded from this that the cooled flow tube was strongly catalyzing recombination of the atoms immediately after transferring, but that some chemical or thermal action of the atomic hydrogen gas would gradually change the nature of the tube so as to decrease the catalytic effect.

This concludes the description of the experimental set-up. Some details of the operation of the system have not been mentioned in this chapter as they fit more naturally with a description of the data which they were used to obtain. These details will appear in the appropriate places in the next chapter.
CHAPTER VI  EXPERIMENTAL RESULTS.

6.1 Observations at 77K.

By filling the outer dewar with liquid nitrogen, and placing helium gas in the inner dewar, the atom detection system would be maintained at 77K. Under these conditions the free induction signal could be observed, with a signal to noise ratio of about 10, after 16,000 pulses were averaged. Measurements were taken with various power levels in the R.F. discharge, which resulted in a change in signal strength, presumably due to a change in the number of hydrogen atoms reaching the detection region.

Fig. 6.1 is a graph of the observed decay rates, \(1/T_2\), as a function of the density of hydrogen atoms, \(n_H\), where this density is calculated from the signal strength in the manner outlined in section 4.3, assuming that the populations of the spin system are in thermal equilibrium at 77K.

The line shown is a least squares fit to the data of the form

\[
\frac{1}{T_2} = \alpha + \beta n_H
\]

with \(\alpha = (127 \text{ sec})^{-1}\), and \(\beta = 1.24 \times 10^{-10} \text{ cm}^3/\text{sec}\). This suggests that there is a transverse relaxation mechanism independent of \(n_H\), and one which is proportional to \(n_H\). The former probably results from interactions between hydrogen atoms and paramagnetic sites on the walls and/or paramagnetic impurities in the gas, while the latter is the result of spin exchange between hydrogen atoms.

If one writes

\[
\frac{d(1/T_2)}{dn_H} = \sigma_{ex} \sqrt{n_{H-H}}/2
\]

(6.1)
Figure 6.1 \( \frac{1}{T_2} \) vs H atom density, \( n_H \).
where $\bar{V}_{H-H}$ is the average relative speed of two atoms, given by

$$\bar{V}_{H-H} = \sqrt{2} \sqrt{\frac{8kT}{\pi m}}$$

(6.2)

and $\sigma_{ex}$ is the spin exchange cross section for $H-H$ scattering, then the value for $\sigma_{ex}$ implied by the data in Fig. 6.1 is $14 \AA^2$.

This value is 60% of the analogous value for $\sigma_{ex}$ found by de Saintfuscien and Audoin, for the zero field hyperfine transition at 77K, which agreed with the calculations of Allison. Although we are observing a different hyperfine transition, the value of $\sigma_{ex}$ should be essentially the same, and it is therefore difficult to explain this discrepancy.

One possible explanation is that the spin system may not be in equilibrium at 77 K, so that the values of $n_H$ for the data in Fig. 6.1 would be incorrect. It is therefore worthwhile to consider the mechanisms by which the spin system may reach thermal equilibrium.

One such mechanism is the spin exchange interaction itself. This mechanism has been modelled by Brown in a high temperature approximation which is valid at 77K. In this treatment, one expresses the product state of two atoms approaching each other as a linear combination of states in which the electrons are in the singlet or triplet state (since these are the eigenstates of the exchange interaction between the two hydrogen atoms). In the course of the collision, the singlet electronic states undergo a different phase shift than the triplet electronic states, and as a result the pair of atoms
are in a linear combination of product states after the collision. By assuming that the difference in phase shifts is sufficiently large that it can be modelled as a random angle, the probability can be calculated for two atoms which were in hyperfine states \( \psi_i, \psi_j \) before the interaction being in states \( \psi_k, \psi_l \) afterward. Thus Brown derives a rate equation for the populations of the hyperfine states. If we let \( c_i \) be the number density of atoms in the \( i^{th} \) energy eigenstate (where the states are numbered in order of increasing energy as in section 2.1), and define \( \rho_i \) by

\[
\rho_i = \frac{4}{n_H} (c_i - c_{ie})
\]

where \( c_{ie} \) is the expected number density at thermal equilibrium, then this rate equation is

\[
\begin{pmatrix}
\dot{\rho}_4 \\
\dot{\rho}_3 \\
\dot{\rho}_2 \\
\dot{\rho}_1
\end{pmatrix} = \frac{S_n_H}{4} \begin{pmatrix}
-1 & 1 & 1 & 1 \\
1 & -(1+\chi) & 1 & -(1-\chi) \\
1 & 1 & -1 & 1 \\
1 & -(1-\chi) & 1 & -(1+\chi)
\end{pmatrix} \begin{pmatrix}
\rho_4 \\
\rho_3 \\
\rho_2 \\
\rho_1
\end{pmatrix}
\]

where \( S \) is a constant depending on the cross section for a collision resulting in a large phase shift, given by

\[
S = \sigma_{ex} \nabla_{h-H}
\]

and \( \chi \) is given by

\[
\chi = 8 \cos^2(\theta) (1 - \cos^2(\theta))
\]

where \( \theta \) is defined in equation (2.8) (at 6481 Gauss, \( \chi = .012 \)).
The general solution to this rate equation is

\[
\begin{pmatrix}
\rho_4(t) \\ 
\rho_3(t) \\ 
\rho_2(t) \\ 
\rho_1(t)
\end{pmatrix} =
\begin{pmatrix}
1 & 0 & 1 & \\
0 & 1 & -1 & \\
-1 & 0 & 1 & \\
0 & -1 & -1 & 
\end{pmatrix}
\begin{pmatrix}
C_1 \\ 
C_2 \exp(-S_n \chi t / 2) \\ 
C_3 \exp(-S_n \chi t) 
\end{pmatrix}
\]

(6.7)

where

\[
C_1 = \left( \rho_{40} - \rho_{20} \right) / 2 \\
C_2 = \left( \rho_{30} - \rho_{10} \right) / 2 \\
C_3 = \left[ \left( \rho_{40} + \rho_{20} \right) - \left( \rho_{30} + \rho_{10} \right) \right] / 4
\]

(6.8)

and \( \rho_{c0} \) is the value of \( \rho_c \) at \( t=0 \).

At typical flow rates of \( 10^{18} \) molecules \( \text{H}_2 \) sec\(^{-1} \), and typical \( \text{H}_2 \) densities in the flow tube of \( 10^{16} \text{cm}^{-3} \), the gas flow velocity was of order 100 cm/sec, and thus the gas would take about 150 msec to flow from the edge of the electromagnet pole to the resonator. By comparison, the equilibration times \( (S_n \chi / 2)^{-1} \), and \( (S_n \chi)^{-1} \), at \( \text{H} \) densities of about \( 2 \times 10^{14} \text{cm}^{-3} \), are about 3 msec, and 20 \( \mu \)sec respectively. Thus it is expected that by the time the gas reaches the resonator, the spin exchange relaxation of the population levels will have proceeded to its fullest extent. These final populations will be:

\[
\begin{align*}
\rho_{4f} &= \left( \rho_{40} - \rho_{20} \right) / 2 \\
\rho_{3f} &= 0 \\
\rho_{2f} &= \left( \rho_{20} - \rho_{40} \right) / 2 \\
\rho_{1f} &= 0
\end{align*}
\]

(6.9)
Thus the populations of levels one and three reach their equilibrium values, while those of levels two and four do not. If we assume that the values of $C_1$, $C_2$, $C_3$, and $C_4$, are $n_H/4$ at $t=0$, then the final populations are

$$
C_{4f} = C_{4e} + (c_{2e} - c_{4e})/2 \\
C_{3f} = C_{3e} \\
C_{2f} = C_{2e} + (c_{4e} - c_{2e})/2 \\
C_{1f} = C_{1e}
$$

The final population difference between levels one and two is thus

$$
C_{2f} - C_{1f} = (c_{2e} - C_{1e}) + (c_{4e} - c_{2e})/2
$$

At 77K, the equilibrium values for the $C_i$'s are:

$$
C_{4e} \equiv (1 - 6.22 \times 10^{-3}) n_H/4 \\
C_{3e} \equiv (1 - 5.80 \times 10^{-3}) n_H/4 \\
C_{2e} \equiv (1 + 5.76 \times 10^{-3}) n_H/4 \\
C_{1e} \equiv (1 + 6.26 \times 10^{-3}) n_H/4
$$

and thus $(C_{2f} - C_{1f})/(C_{2e} - C_{1e}) = 13.0$ ; that is the final population difference between levels one and two is 13 times greater than it would be at thermal equilibrium.

This enhanced population would cause an enhanced magnetic resonance signal in the same proportion. However, as is shown in
Appendix A, this enhancement disappears after repetitive $\pi/2$ pulses. This occurs because the $\pi/2$ pulse averages the populations of states one and two, and the spin exchange relaxation then returns the population of level one to equilibrium, leaving the population of level two with about half its original difference from equilibrium. The end result of this process is the following:

\[ C_4 \text{ (rep. pulse)} = C_{4e} + (C_{ae} - C_{1e}) \]
\[ C_3 \text{ (rep. pulse)} = C_{ae} \]
\[ C_2 \text{ (rep. pulse)} = C_{1e} \]
\[ C_1 \text{ (rep. pulse)} = C_{1e} \]

That is, when one averages the above $C_1$ and $C_2$ values with a $\pi/2$ pulse, and allows spin exchange relaxation to proceed to its fullest extent, the values of the $C_i$ are back to what they were before the $\pi/2$ pulse. The difference between levels one and two before the $\pi/2$ pulse under these conditions is

\[ (C_2 - C_1) \text{ rep. pulse} = 0 \]  

(6.14)

Thus although there is clearly the possibility of a signal enhancement resulting from spin exchange, the degree of this enhancement should be strongly dependent on the pulse repetition rate. When the rate is slow enough that every atom flowing down the tube experiences only one $\pi/2$ pulse (which requires a pulse interval of 10 msec), the signal should be enhanced 13 times, while at repetition rates causing several $\pi/2$ pulses
per atom, the enhancement should rapidly disappear. Experimentally, no significant variation in signal strength was found in varying the pulse interval from 200μsec to 10 msec. Thus it seems that spin exchange is not the only relaxation mechanism present.

The only other mechanisms we have thought of are interactions between the hydrogen atoms and paramagnetic sites on the walls of the flow tube. Such interactions with unlike spins would cause complete equilibration of the spin system. However, it seems doubtful that this process could significantly contribute to the observed relaxation rates. The most probable paramagnetic gas impurity is O₂, which has spin exchange cross section 25.1 X 10⁻¹⁶ cm², and would therefore have to be about as abundant as hydrogen atoms, (i.e. several molecules O₂ per thousand molecules H₂), to significantly contribute. Since we have no reason to expect impurities at this very high level, this possibility can be ruled out. A similar problem exists with paramagnetic wall sites. Since the atoms diffuse to the teflon coated wall in times somewhat greater than T₂, the teflon surface would have to be almost completely covered with paramagnetic sites to significantly contribute, which seems very unlikely.

It is possible that such interactions with unlike spins would weakly contribute to the relaxation, and that in combination with spin exchange relaxation there could be a net signal enhancement less dependent on pulse rate. Another explanation for our small value for σex is an error in the spectrometer calibration procedure. At present the problem remains unresolved.
6.2 Data Taken at 4.2 K With No Buffer Gas.

Upon transferring liquid helium into the inner dewar, the magnetic resonance signal would disappear and then after a few minutes it would gradually return, as was described in section 5.4. Although the signal was stronger at liquid helium temperature, the actual number density calculated, assuming thermal equilibrium of the spin system at 4.2K, had decreased to $3 \times 10^{13} \text{ cm}^{-3}$. $T_2$ for this signal was less than 50 $\mu$sec. Although this short $T_2$ could arise from spin exchange, the necessary cross section would have to be very large, which would contradict the theoretical prediction of Allison$^{19}$. Another explanation was that the atoms were diffusing out of the resonator or against the wall of the flow tube, since at these temperatures the H$_2$ gas is frozen out on the wall of the flow tube, and such diffusion times would therefore be quite short.

Since the mean free path of the atoms at densities of $3 \times 10^{13} \text{ cm}^{-3}$ is of the order of 30 cm, and thus much longer than the sample region, the characteristic time, $t$, for them to leave the resonator or collide with the flow tube wall is given roughly by

$$t \approx \frac{l}{\bar{v}}$$  \hspace{1cm} (6.15)

where $l$ is a characteristic length of the sample region, and $\bar{v}$ is the average speed of the atoms, which is

$$\bar{v} = \sqrt{\frac{8kT}{\pi m}}$$  \hspace{1cm} (6.16)
Letting \( \lambda = \text{lcm} \), the value of \( t \) obtained is about 50 \( \mu \text{sec} \), which strongly suggested that such diffusion was the mechanism behind the observed \( T_2 \).

To test this hypothesis, a small quantity of helium gas was added to the sample region via the pumping line, with the diffusion pump closed off. The result was a large increase in \( T_2 \), as would be expected if diffusion was the decay mechanism, since the mean free path for the atoms would decrease upon addition of helium "buffer" gas, thus lengthening diffusion times. Fig. 6.2 shows a series of free induction decays at various buffer gas densities.

In section 4, detailed discussion of the results obtained by varying buffer gas density are presented. Before presenting these, however, it is useful to describe the analysis which was performed of the expected relationship between \( T_2 \) and buffer gas density.

6.3 Analysis of the Diffusion Problem.

In the next section, it will be shown that the decay rate of the free induction signal, \( 1/T_2 \), and a frequency shift of the signal, \( \Delta \omega \), both occurred in direct proportion to the diffusivity of the hydrogen atoms in the buffer gas. In this section a model is presented to explain this behaviour, and a description is given of a computer simulation of that model. The results of this simulation will be employed in the analysis in section 4.

In the model, the atoms diffuse through the buffer gas, out of the resonator region and/or against the wall of the flow
Figure 6.2  Free induction decays at 4.2 K with various helium buffer gas densities.
tube. It is postulated that during the time an atom is in contact with the wall of the flow tube (which is probably coated with solid $H_2$), it undergoes a phase shift $-\Delta$. This phase shift can produce an effective frequency shift of the total free induction signal, and will also cause a decay of that signal since atoms which have accumulated different amounts of phase shift become out of phase with one another. These phase shifts result from the change in the contact hyperfine interaction due to collisions with the $H_2$ coated walls. (This same effect leads to a lowering of the hyperfine frequency for $H$ trapped in solid $H_2$.) The collision with the wall is not instantaneous since the atom can "stick" or stay close to the wall for some time. We model this effect by saying that the atom has an equal probability of leaving the surface per unit time, and thus that the probability distribution for the magnitude of the phase shift is given by

$$P(\Delta) = \Delta_0^{-1} \exp(-\Delta/\Delta_0)$$ (6.17)

In this model, the values for $T_2$ and $\Delta \omega$ are determined as follows. Let $\phi_i(t)$ be the total accumulated phase shift for the $i^{th}$ atom, and let $\Theta_i(t)$ be a function which is 0 if the $i^{th}$ atom is not in the resonator at time $t$, and 1 if it is. Then the relative amplitude of the free induction signal, $A(t)$, is given by

$$A(t) = \left[ \left( \sum_i O_i(t) \sin(\phi_i(t)) \right)^2 + \left( \sum_i O_i(t) \cos(\phi_i(t)) \right)^2 \right]^{1/2}$$ (6.18)
and the net phase shift of the free induction signal, \( \varphi(t) \), is given by:

\[
\varphi(t) = \tan^{-1} \left( \frac{\sum_i \phi_i(t) \sin(\phi_i(t))}{\sum_i \phi_i(t) \cos(\phi_i(t))} \right)
\]  

(6.19)

\( T_2 \) is then taken to be the time at which the amplitude has decayed to \( 1/e \), that is

\[
A(T_2) = e^{-1}
\]  

(6.20)

Now it will be seen that in the computer simulation \( \varphi(t) \) increases quite linearly with time, (see Fig. 6.3) and it is thus reasonable to speak of the effective frequency shift, \( \Delta \omega \), as

\[
\Delta \omega = \frac{d \varphi(t)}{dt}
\]  

(6.21)

More precisely, since we measured frequency by counting the total phase shift occurring over a time of order \( T_2 \) (see section 4.4), the best definition of \( \Delta \omega \) is given by:

\[
\Delta \omega = \frac{\varphi(T_2)}{T_2}
\]  

(6.22)

In simulating the above model a great simplification can be made by assuming that the mean free path of the hydrogen atoms is quite a bit smaller than the sample region, so that the movement of the atoms is governed by the diffusion equation. This assumption is valid for all of the measurements presented in the next section. If \( n^* \) is the number density of hydrogen atoms which received the \( \pi/2 \) pulse, the diffusion equation is
\[ h^* = D \nabla^2 n^* \]  
(6.23)

where \( D \) is the diffusivity of the hydrogen atoms in the buffer gas, and the boundary conditions are

\[ (\nabla n^*) \cdot \hat{n} = 0 \]  
(6.24)

where \( \hat{n} \) is the normal vector to any impermeable surface.

The value of \( D \) may be expressed in terms of a diffusion cross section, \( Q_0 \), as

\[ b = \left( \frac{3\pi}{32} \right) \sqrt{\frac{V_R}{n_b}} Q_0 \]  
(6.25)

where \( V_R \) is the average relative speed of hydrogen atoms and buffer gas particles, and \( n_b \) is the buffer gas density.

Although we do not solve the diffusion equation directly, (instead we model the actual motion of the atoms), it is instructive to study the form of this equation. Since the equation is linear, it is possible to scale a solution for one set of initial conditions and diffusion constant to a set of initial conditions with the same geometry, but different size, and/or with different diffusion constant. If we let \( n_1^*(r, t) \) be the solution to the problem with initial condition \( n_1^*(r, 0) \), boundary defined by \( f_1(r) = 0 \), and diffusion constant \( D_1 \), and we seek a solution to \( n_2^*(r, t) \), \( f_2(r) = 0 \), \( D_2 \), then if \( n_2^*(r, 0) = n_1^*(ar, 0) \) and \( f_2(a r) = f_1(r) \); the solution \( n_2^*(r, t) \) is given by

\[ n_2^*(r, t) = n_1^*(a r, \frac{D_2}{D_1 a^2} t) \]  
(6.26)

In other words, if one scales every feature of the system by
the same factor, and/or changes the diffusion constant, the characteristic times and rates simply change by an appropriate factor, and the evolution of $n^*$ is of the same basic form. Thus we can employ a computer simulation in a region with the same geometry as that of the experimental sample region, but with arbitrary size and diffusion constant, and apply the result to the experimental region.

In particular, the above considerations imply that the diffusion controlled $T_2$ for a given geometry should be of the form

$$T_2 = \alpha \frac{H^2}{D}$$

(6.27)

where $H$ is a characteristic size, (which we will take for convenience to be the height of the resonator), and $\alpha$ is a dimensionless factor which may depend on the value of $\Delta_0$. The value of $\alpha$ can thus be obtained from the computer simulation, and applied to the experimental results.

In the computer simulation technique, each atom is represented as a point with integer coordinates in three dimensions, and has an additional real variable to record its total accumulated phase shift. The coordinates of each atom undergo a random change at each iteration of the program. The change consists of moving either plus or minus one unit in the $x$, $y$, and $z$ directions, the choice in each direction being made by a random number generator. The flow tube was modelled as a semi-infinite tube extending in the positive $z$ direction, which had a cross section of $N \times N$ units, where $N$ could be any
odd integer. \( N^3 \) atoms were initially "placed", one on each of the sites in the \( N \) bottom layers of the flow tube, so as to model the original distribution of atoms in the resonator which receive a \( \pi/2 \) pulse. (The value of \( N \) was chosen to be large enough to reduce random noise and eliminate the effect of discrete steps. \( N=13 \) was found to be sufficient.) Whenever a random step would cause an atom to pass through the wall of the flow tube, the component of the step responsible for this would not be taken. In addition, the phase of the atom would be changed an amount, \(-\Delta\), where \( \Delta \) was randomly chosen according to the formula

\[
\Delta = -\Delta_0 \ln(\text{RND})
\]

(6.28)

where RND is a random number between 0 and 1. It is easily shown that the probability distribution for this \( \Delta \) is that given in (6.17). At the end of each iteration, the computer would calculate \( \Delta \) and \( \vec{\phi} \) as described in (6.18) and (6.19), and print them. Figure 6.3 shows a plot of \( \Delta(t) \) and \( \vec{\phi}(t) \) for various values of \( \Delta_0 \).

The effective diffusion constant corresponding to the random walk procedure used in this program is easily determined, by considering the mean square distance an atom would travel after \( n \) random steps with no impermeable boundaries, and comparing to the result predicted from the diffusion equation. Since

\[
\langle r^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle
\]

(6.29)
Figure 6.3  Computer simulation results for \( \ln A \) and \( \bar{\theta} \) vs \( t \), for various values of \( \Delta_0 \).
and the walk procedure is symmetrical and independent in the three coordinates,

\[
\langle r^2 \rangle = 3 \langle x^2 \rangle \tag{6.30}
\]

The value of \( \langle x^2 \rangle \) is most easily obtained by means of the central limit theorem, which states that if one adds \( n \) random variables, each with variance \( \sigma^2 \), then the variance of the sum will be \( n \sigma^2 \). In our case, the probability distribution for the random variable is

\[
P(\Delta x) = \frac{1}{2} \delta(\Delta x+1) + \frac{1}{2} \delta(\Delta x-1) \tag{6.31}
\]

which has variance \( \sigma^2 = 1 \). Thus the value for \( \langle x^2 \rangle \) is \( n \), and \( \langle r^2 \rangle = 3n \). Now in the solution to the diffusion equation with a delta function density distribution at the origin at \( t=0 \), one finds

\[
\langle r^2 \rangle = 6Dt \tag{6.32}
\]

and since \( \langle r^2 \rangle = 3n \), and \( t=n \), the effective diffusion constant in this computer simulation is \( D=1/2 \). For the purpose of determining \( \alpha \), we note that the height of the resonator, \( H \), is \( N \) units in this simulation, and hence

\[
\alpha = \frac{T_2 D}{H^2} = \frac{T_2}{2N^2} \tag{6.33}
\]

where \( T_2 \) is measured in number of iterations.

As can be seen in Fig. 6.3 \( \Phi(t) \) increases quite linearly in time, and so it is meaningful to speak of a frequency shift \( \Delta\omega \) defined as
Figure 6.4  Computer simulation values for $T_2 \Delta \omega$ and $\alpha$ vs $\Delta_0$. 
For comparison to experimental data, it is useful to determine the dimensionless quantity $T_2 \Delta \omega$:

$$T_2 \Delta \omega = \overline{\varphi}(T_2)$$  \hfill (6.35)

It would seem reasonable that this quantity would depend only on the nature of the phase shift on the walls, since the number of such phase shifts in a time $T_2$ should be independent of the diffusion rate and absolute size of the system. This fact was verified by changing the value of $N$ (hence lengthening $T_2$), and finding that neither $\overline{\varphi}(T_2)$ nor $\alpha$ were significantly changed.

Thus our computer simulation had one variable parameter, $\Delta_a$, and could be used to predict the dimensionless quantities $\overline{\varphi}(T_2)$ and $T_2 \Delta \omega$ for this geometry. Fig. 6.4 shows a plot of $\alpha$ and $T_2 \Delta \omega$ vs $\Delta_a$. These results will be compared to the experimental data in the next section.

6.4 Experimental Results with Buffer Gas at Low Temperatures.

The values of $T_2$ obtained from the free induction decays are shown as a function of buffer gas density in the log-log plot in Fig. 6.5. The circles in this graph indicate data which were taken with helium buffer gas, which was added via the pumping line with the diffusion pump closed off, and the crosses indicate data taken with $H_2$ buffer gas, obtained by allowing the solid $H_2$ coated detection region to warm
Figure 6.5 Log-log plot of $T_2$ vs $n_B$. Circles represent measurements with He buffer gas at 4.2K, the crosses are for $H_2$ buffer gas for 5.6<T<8.4K; the solid line represents a linear dependence on $n_B$. 
slowly between 5 and 9 K (after all the liquid helium in the dewar had boiled off), so as to produce a vapor pressure of $H_2$. For both the He and $H_2$ buffer gases, the maximum density which could be used was determined by the fact that the magnetic resonance signal would disappear above a certain density, presumably because the atoms were unable to diffuse through the buffer gas to the resonator before recombining.

In the case of He buffer gas, the density, $n_B$, was determined by measuring the gas pressure in the pumping line with the ion gauge on the diffusion pump (which had been calibrated against a Varian 843 gauge of 2.2% accuracy), and calculating the corresponding density in the detection region. In performing this calculation, one must take into account the thermomolecular effect, \(^{22}\) which for a pumping line of our dimension, takes the form

$$\frac{P_a}{P_b} = \sqrt{\frac{T_a}{T_b}}$$  \hspace{1cm} (6.36)

(where $T_a$ and $T_b$ are the temperatures in the two regions) and thus

$$n_B(T_a) = \sqrt{\frac{T_b}{T_a}} n_B(T_b) = \frac{P}{k\sqrt{T_a T_b}}$$  \hspace{1cm} (6.37)

where we have assumed that the He behaves like an ideal gas. The density of $H_2$ buffer gas was determined by measuring the temperature of the detection region via the calibrated carbon resistor thermometer (see section 5.4), and inferring $n_B$ from the known vapour pressure of $H_2$. \(^{23}\)

According to the diffusion discussion of the last section, we expect that $T_2$ should be inversely proportional to $D$, and
hence proportional to $n_b$. For both the He and $H_2$ buffer gas results in Figure 1, it can be seen that lines of unit slope on the log-log plot fit the data well over two decades of buffer gas density, in good agreement with the diffusion model. (The apparent deviation from this relationship of the highest density $H_2$ buffer gas points will be discussed below.)

Frequency shift data were obtained by varying the magnetic field about the value $H_0$, in order to determine the experimental minimum frequency, $f_{\min}$. Some of these results are shown in Fig. 6.6, for $n_b(\text{He})=(2-3)\times10^{14}$ cm$^{-3}$ (circles), and $n_b(\text{He})=10^{15}$ cm$^{-3}$ (crosses). Both sets of data fit a parabola of the predicted curvature, centered about essentially the same value of magnetic field. It is clear from this data that the experimental minimum frequency, $f_{\min}$, is negatively shifted from the theoretical value $f_o$, by an amount which is pressure dependent. The pressure dependence of this shift was found, within experimental error, to be the same as that of the decay rate, as indicated in Fig. 6.7, where the difference $f_o-f_{\min}$ is plotted as a function of $1/T_2$. The data can be fit with a straight line through the origin with slope such that

$$2\pi(f_o-f_{\min})T_2=T_2\Delta\omega = 1.3 \pm 0.4.$$  

The fact that $T_2\Delta\omega$ is constant for this data, and that $T_2 \propto n_b$ strongly suggests that the diffusion model of the previous section is correct. In Fig. 6.4, it can be seen that $T_2\Delta\omega$ in the simulation has a broad maximum at $\Delta_o \approx 2$. The experimental value of $1.3 \pm 0.4$ would be consistent with $1 < \Delta_o < 3$. Further information on the value of $\Delta_o$ was obtained by observing the shape of the decay curve $\ln A(t)$ vs $t$. With $\Delta_o = 1$, the simulation decay curve was rather
Figure 6.6 Resonance frequency as a function of magnetic field, plotted as $f-f_0$ vs $H-H_0$ where $f_0=765 \ 483 \ 208$ Hz and $H_0=6481.9$ G.

- $n_B(\text{He})=2.5 \times 10^{14}$ cm$^{-3}$
- $n_B(\text{He})=1.0 \times 10^{15}$ cm$^{-3}$
Figure 6.7 $f_0 - f_{\text{min}}$ vs $1/T_2$ for $\text{H}_2$ (dots) and $\text{He}^4$ (squares) buffer gas data.
non-exponential, as would be expected for a pure diffusion problem, while for $\Delta_0 = .3$, the decay was essentially exponential. In the experimental data, it was found that the decays with He buffer gas displayed the non-exponential appearance of the simulations with $\Delta_0 = .1$, while those with $H_2$ buffer gas were quite exponential. Examples are shown in Fig. 6.8. Thus it appears that the nature of the wall of the flow tube was different in the two cases (possibly because of the slightly different temperatures, leading to different values of $\Delta_0$.

Knowing $\Delta_0$, $\alpha$ can be determined from the data in Fig. 6.4, which can be employed with equations (6.25) and (6.27) to obtain

$$Q_0 = \frac{3\pi}{32} \frac{v_R}{\alpha} \frac{T_2}{n_B}$$

(6.38)

where $v_R$, the average relative speed of a hydrogen atom and buffer gas particle, is given by

$$v_R = \sqrt{\frac{8kT}{\pi m_r}}$$

(6.39)

Using $\Delta_0 = .1$ for the helium data, which yields $\alpha = .25$, and the value $T_2/n_B = 1.4 \times 10^{-18} \text{cm}^3 \text{sec}$ for the top line in Fig. 6.5, we obtain a value for $Q_0$ for H in He at 4.2 K of about 500 A.$^2$. For $H_2$, letting $\Delta_0 = .3$, we found $\alpha = .09$, and using the value $T_2/n_B = 2.6 \times 10^{-19} \text{cm}^3 \text{sec}$ for the bottom curve in Fig. 6.5, we obtain a value for $Q_0$ for H in $H_2$ in the range of 5-9 K of about 250 A.$^2$.

In view of the uncertainty in the precise nature of the
Comparison of experimental decay shapes with computer simulation results.

Figure 6.8 Comparison of experimental decay shapes with computer simulation results.
phase shifts at the walls, and slight differences between the actual flow tube geometry and that of the simulation, these results are not expected to be very accurate. However, it would seem unlikely that our calculated values could be incorrect by more than a factor of two, and in this light the very large values of $Q_0$ we obtained are extremely surprising, and would imply resonances in the $H-He$ and $H-H_2$ cross sections at low energies. However, at least for $H-He^4$, the existence of resonances is inconsistent with the measurements of Toennies, Welz, and Wolf$^{24}$, who obtain about 40 $\text{Å}$ for the total cross section at low energies. It is very unlikely that the properly averaged thermal cross section would be more than twice this value. Nevertheless, we have been unable to find inconsistencies in our data, or any alternative explanation for the long $T_2$'s which occur in proportion to apparently small quantities of buffer gas.

The effect of spin exchange, which should produce a decay rate independent of buffer gas density, was not apparent for most of the low temperature data. In Fig. 6.5, however, it can be seen that at the highest buffer gas densities, (with $H_2$ buffer gas), the data curve away from the linear relationship. The dotted curve is of the form

$$\frac{1}{T_2} = \frac{1}{a n_b} + \frac{1}{T_2^{ex}}$$

(6.40)

where $a$ is the value of $T_2/n_b$ for the line passing through the $H_2$ buffer gas data, and $T_2^{ex} = 12 \text{ msec}$. The reasonably good fit suggests that the quantity $T_2^{ex}$ represents the $T_2$ which would
result purely from spin exchange. The value of $n_H$, determined from the signal strength, was $3 \times 10^{13} \text{cm}^{-3}$, and using the same procedure as in section 6.1 we find the spin exchange cross section $\sigma_{ex}$ at the temperature involved ($\sim 8\text{K}$), to be $0.9 \text{Å}$. This result is consistent with extrapolations of the results of Allison$^{19}$, and is in good agreement with the calculation of Berlinsky$^{20}$. Of course it is possible that there is some other buffer gas density independent decay mechanism and that $\sigma_{ex}$ is therefore smaller. In any case, it is clear that $\sigma_{ex}$ decreases by at least a factor of 15 as the temperature is lowered from 77 to 8 K.
CHAPTER VII  SUMMARY

Atomic hydrogen gas was produced by dissociating $\text{H}_2$ in a room temperature R.F. discharge, and was piped 1 meter into a cryogenic system which could cool the gas to temperatures in the range of 77-1 K. The atoms were detected by means of pulsed magnetic resonance. The transition observed was between the two lowest hyperfine levels of the $1s$ atom, in a field of 6.5 kG, where the resonance frequency has a minimum value of 765 MHz.

At 77 K, the effects of spin exchange relaxation were observed. The spin exchange cross section was calculated from the observed proportionality constant between the signal decay rate and the hydrogen atom number density. The value of $14 \text{Å}^2$ obtained is 60% of the theoretical value$^{19}$, which has previously been experimentally confirmed$^7$. It is possible that this discrepancy resulted from the populations of the hyperfine states differing from their thermal equilibrium values, as is possible if spin-exchange between hydrogen atoms is the dominant relaxation mechanism. However, such an explanation would appear to contradict the observed independence of the signal strength and pulse repetition rate for rates less than about $1/2T_2$. At present the problem remains unresolved.

At liquid helium temperatures the effects of spin-exchange were much smaller, and diffusion out of the resonator was the dominant $T_2$ mechanism. Decay rates were measured as a function of the density of $\text{He}_4$ buffer gas at 4.2 K and $\text{H}_2$ buffer gas in the range of 5-9 K. In addition a shift of the minimum frequency was observed, and was found to be proportional to the decay rate.
These results were explained by a model in which the atoms diffused through the buffer gas, out of the resonator and/or against the wall of the flow tube, in which case they would undergo a random phase shift. The one free parameter in this model was the mean magnitude of the phase shift. In a computer simulation of the model, we obtained good fits to the decay shapes of the experimental signals, as well as the correct ratio of frequency shift to decay rate.

This analysis implied very low diffusivities for H in He\(^4\) and H\(_2\), and hence very large diffusion cross sections. At 4.2 K in He\(^4\) buffer gas, the cross section obtained was 500 Å\(^2\), while at 5-9 K in H\(_2\), it was 250 Å\(^2\). Although these results are not expected to be extremely accurate, it seems unlikely that they are off by more than a factor of two, and these large values are therefore quite surprising, and warrant further study.

The effects of spin-exchange were observed at 8 K with our highest densities of buffer gas. The cross section calculated was .9 Å\(^2\), which is consistent with extrapolations of the results of Allison\(^{19}\), and is in good agreement with the calculations of Berlinsky\(^{20}\).

From a practical point of view, it has been established that at low densities atomic hydrogen gas can be transported distances of order 1 meter, cooled to liquid helium temperatures, and studied by means of magnetic resonance. It is hoped this information will be useful for future work in the field of spin-polarized hydrogen.
APPENDIX A: POPULATIONS OF STATES RESULTING FROM REPEATED $\pi/2$ PULSES WITH SPIN-EXCHANGE RELAXATION.

We wish to consider the result of performing the following operation $N$ times: a $\pi/2$ pulse is applied, equalizing the populations of states 1 and 2, and the system then equilibrates to the fullest extent possible via spin-exchange relaxation.

These operations can be conveniently discussed in matrix notation. We express the state populations in terms of the quantities $\rho_i$ defined in equation (6.3). The operation of a $\pi/2$ pulse on states 1 and 2 can be expressed as

$$
\begin{pmatrix}
\rho_{1,n+1} \\
\rho_{2,n+1} \\
\rho_{3,n+1} \\
\rho_{4,n+1}
\end{pmatrix} = 
\begin{pmatrix}
0 \\
0 \\
0 \\
0
\end{pmatrix} + 
\begin{pmatrix}
1 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 \\
0 & 0 & \frac{1}{2} & \frac{1}{2} \\
0 & 0 & \frac{1}{2} & \frac{1}{2}
\end{pmatrix} 
\begin{pmatrix}
\rho_{1,n} \\
\rho_{2,n} \\
\rho_{3,n} \\
\rho_{4,n}
\end{pmatrix} 
$$

(A.1)

where

$$a = \frac{i}{n_{11}} (c_{2e} - c_{1e})$$

For convenience, we will define the operator causing this operation to be $O_{\pi/2}$, expressed as

$$O_{\pi/2} = 
\begin{pmatrix}
0 \\
0 \\
0 \\
0
\end{pmatrix} + 
\begin{pmatrix}
1 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 \\
0 & 0 & \frac{1}{2} & \frac{1}{2} \\
0 & 0 & \frac{1}{2} & \frac{1}{2}
\end{pmatrix}$$

(A.2)

It is understood the operator is to be applied as in A.1. (It is easily verified that $(O_{\pi/2})^N = O_{\pi/2}$ - equalizing the populations of states 1 and 2 $N$ times is equivalent to equalizing them once, as expected.)

Similarly, the operation of equilibration via spin-exchange to the fullest possible extent, as described in
equations (6.9), can be expressed as

\[
\mathcal{O}^{\text{spin}} = \begin{pmatrix}
0 & 1/2 & 0 \\
0 & 0 & 0 \\
-1/2 & 0 & 0 \\
0 & 0 & 0 \\
\end{pmatrix}
\] (A.3)

(Again it is easily verified that \(\mathcal{O}^{\text{spin}}\)^N = \(\mathcal{O}^{\text{spin}}\), as expected.)

Let us evaluate explicitly our combined operation,

\[
\hat{\mathcal{R}}_{n+1} = (\mathcal{O}^{\text{spin}} \mathcal{O}_{\pi/2}) \hat{\mathcal{R}}_n = \begin{pmatrix}
0 & 1/2 & 0 \\
0 & 0 & 0 \\
-1/2 & 0 & 0 \\
0 & 0 & 0 \\
\end{pmatrix}
\begin{pmatrix}
0 \\
1 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 \\
0 & 0 & 1/2 & 0 \\
\end{pmatrix}
\begin{pmatrix}
\rho_{1n} \\
\rho_{2n} \\
\rho_{3n} \\
\rho_{4n} \\
\end{pmatrix}
\] (A.4)

\[
\Rightarrow \hat{\mathcal{R}}_{n+1} = \begin{pmatrix}
0 \\
1/2 & 0 & -1/2 \\
0 & 0 & 0 \\
0 & 0 & 0 \\
\end{pmatrix}
\begin{pmatrix}
0 & 1/2 & 0 \\
0 & 0 & 0 \\
-1/2 & 0 & 0 \\
0 & 0 & 0 \\
\end{pmatrix}
\begin{pmatrix}
\rho_{1n} \\
\rho_{2n} \\
\rho_{3n} \\
\rho_{4n} \\
\end{pmatrix}
\] (A.5)

Define M, V as follows:

\[
M = \begin{pmatrix}
0 & 1/2 & 0 \\
0 & 0 & 0 \\
-1/2 & 0 & 0 \\
0 & 0 & 0 \\
\end{pmatrix}
\] (A.6)

\[
\hat{V} = \begin{pmatrix}
0 \\
0 \\
-1/2 \\
0 \\
\end{pmatrix}
\]

so that \(\mathcal{O}^{\text{spin}} \mathcal{O}_{\pi/2} = \hat{V} + M\).

The application of this operation several times can be easily expressed in this notation:
\[
\begin{align*}
\left( O_{\text{spin}} \times O_{\pi/2} \right)^1 &= \vec{V} + M \\
\left( O_{\text{spin}} \times O_{\pi/2} \right)^2 &= \vec{V} + M(\vec{V} + M) = \vec{V} + M\vec{V} + M^2 \\
\left( O_{\text{spin}} \times O_{\pi/2} \right)^3 &= \vec{V} + M(\vec{V} + M(\vec{V} + M)) = \vec{V} + M\vec{V} + M^2\vec{V} + M^3 \\
n\text{etc.}
\end{align*}
\]

Clearly,
\[
\left( O_{\text{spin}} \times O_{\pi/2} \right)^N = \vec{V} + \left( \sum_{n=1}^{N-1} M^n \right) \vec{V} + M^N
\]

This expression is easily evaluated, since \( M \) has the property that
\[
M^n = \left( \frac{3}{4} \right)^{n-1} M
\]

Thus
\[
\left( O_{\text{spin}} \times O_{\pi/2} \right)^N = \vec{V} + \left( \sum_{n=1}^{N} \left( \frac{3}{4} \right)^{n-1} \right) M\vec{V} + \left( \frac{3}{4} \right)^{N-1} M
\]

Summing the geometric series, we obtain
\[
\left( O_{\text{spin}} \times O_{\pi/2} \right)^N = \vec{V} + 4 \left( 1 - \left( \frac{3}{4} \right)^N \right) M\vec{V} + \left( \frac{3}{4} \right)^{N-1} M
\]

This expression rapidly converges as \( N \to \infty \) to
\[
\lim_{N \to \infty} \left( O_{\text{spin}} \times O_{\pi/2} \right)^N = 4 M \vec{V} + \vec{V}
\]

Substituting the expressions for \( M, \vec{V} \) in (A.6), we obtain
\[
\lim_{N \to \infty} \left( O_{\text{spin}} \times O_{\pi/2} \right)^N = \begin{pmatrix} 2a \\ 0 \\ -2a \end{pmatrix}
\]
Thus \( \hat{\rho}_{\text{rep. pulse}} = \begin{pmatrix} 2a \\ 0 \\ -2a \\ 0 \end{pmatrix} \), (independent of \( \rho_o \)) \hfill (A.15)

That is, regardless of what the \( \rho_z \) values were initially, the result of repeating this \( \pi/2 \) pulse - spin exchange relaxation operation many times will be that expressed in (A.15). It is interesting that neither \( \pi/2 \) pulsing nor spin exchange relaxation alone "erase the past" in this manner.

Let us now evaluate the population difference between states 1 and 2 corresponding to \( \hat{\rho}_{\text{rep. pulse}} \). Employing equation (6.3), we have

\[
C_i = \frac{\rho_{\text{rep. pulse}}}{4} + C_{ie} \hfill (A.16)
\]

and thus

\[
(C_2-C_1)_{\text{rep. pulse}} = \frac{n_H}{4} (\rho_{\text{rep. pulse}})_{\text{rep. pulse}} + (C_{2e} - C_{1e}) \hfill (A.17)
\]

Employing (A.15) and the definition of \( a \) in (A.1), we obtain

\[
(C_2-C_1)_{\text{rep. pulse}} = 0 \hfill (A.18)
\]
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