SPIN RELAXATION AND RECOMBINATION
IN ATOMIC HYDROGEN GAS
AT TEMPERATURES AROUND 1 K

by
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ABSTRACT

An experiment for studying a gas of atomic hydrogen at temperatures between 0.9 K and 1.3 K is described. The field dependence of the recombination rate of H atoms into $H_2$ molecules and the spin-exchange cross-section are investigated. Atoms are produced \textit{in situ} in a low temperature discharge and are confined in a pyrex cell. The walls of this cell are covered with a film of superfluid $^4$He for preventing recombination. The detection and the study of the hydrogen atoms is done using the technique of pulsed magnetic resonance between the lowest two hyperfine levels of the ls hydrogen atoms. The frequency is about 765.5 MHz and corresponds to a shallow minimum in the difference between the lowest two hyperfine levels, which occurs at 6481 kGauss.

A simple model is also derived for explaining the field dependence of the recombination in the presence of a relatively large $^4$He density. In fact, due to the vapour pressure, the helium density will be above $10^{18}$ atoms/cm$^3$ in the range of temperatures in which we are interested, while the density of hydrogen atoms will be about $10^{11}-10^{12}$ atoms/cm$^3$. The relaxation mechanism assumed is spin-exchange. The parameters of the model are fit to the existing data. It is found in particular that the asymptotic behavior of the hyperfine populations depends sensitively on the initial populations.
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In low temperature physics, it is possible to observe striking phenomena, such as superconductivity or superfluidity, which give direct evidence of the quantum nature of the system and which become evident only when most of the thermal energy has been removed. A good example of such a system is helium, for which there exist two isotopes, namely $^3$He and $^4$He. The former is a fermion and, thus, obeys Fermi-Dirac statistics, and the latter is a boson and obeys Bose-Einstein statistics. Therefore, the collective behavior is quite different in the two cases. In fact, liquid $^4$He has a superfluid state, which occurs at temperatures below $2.17^\circ$K, the $\lambda$ point, whereas $^3$He remains a normal liquid down to about 2 mK where it becomes a superfluid due to Cooper pairing (Legget 1980). Superfluidity is the signature of Bose-Einstein condensation, a consequence of Bose-Einstein statistics. It occurs when the particles start to populate the lowest energy state, whence the word condensation.

In 1959, it was pointed out by Hecht (Hecht 1959) that helium was not unique in that respect, and that hydrogen (H) and tritium (T) atoms could also show superfluid properties, since they are bosons. By contrast to helium, however, a gas of hydrogen atoms is highly reactive. It will not only react with the walls of most containers, but it is also unstable against recombination into $H_2$ molecules. Hydrogen atoms will bind to any material and, if the binding is not chemical, recombination into $H_2$ will quickly
follow. This high reactivity has always complicated the problem of experimentally observing the thermodynamic properties of H atom gas. Only recently has it been possible to stabilize an atomic H gas at reasonable densities, where "stabilized" means that the atom density decays slowly enough that there is time for making experiments (see Nature, Sept. 1979, or Physics Today, June 1980).

Binding to the wall can be reduced by coating the inner surface of the containing vessel with a material for which the binding energy is much smaller than the average kinetic energy of the atoms. For instance, teflon is frequently used as a coating at high temperature since its binding energy is about 255°K (Zitzewitz 1970). The least binding solid surface is either molecular hydrogen (Crampton 1980) or possibly solid neon. However, the binding energy of H atoms on solid H\textsubscript{2} is still high by cryogenic standards (\sim 35°K). For studying H atom gas in a much lower range of temperatures, it is necessary to have a film of superfluid \(^4\text{He}\) covering the surfaces (Hardy et al. 1980, or Silvera and Walraven 1980). The binding energy on \(^4\text{He}\) has recently been measured to be 0.93°K \pm 0.05°K (Morrow et al.), and this result is consistent with the calculations of Edwards and Mantz (Edwards and Mantz 1980). Thus, the effect of the binding will become important only well below 0.9°K, and it is now a standard procedure to use superfluid \(^4\text{He}\) for preventing binding to the walls. However, unless the temperature is well below 1°K, there remains a substantial amount of helium gas due to the vapor pressure and this will cause bulk recombination as we shall see later.

Bulk recombination is reduced at low temperatures by the
application of a large magnetic field. This was evidenced experimentally by the work of the Amsterdam group where fields up to 70 kGauss at temperatures around 0.3°K were used (see Silvera and Walraven 1980). This approach for stabilizing atomic hydrogen is based on the fact that the interaction between two hydrogen atoms depends sensitively on their total electronic spin, denoted S. For S=1, the potential U(R), where R is the internuclear distance, is basically repulsive (except for a shallow minimum at R = 4 Å due to the dispersion forces), while for S=0 the potential has a repulsive core and a strong attractive tail, with a deep minimum (4.7 eV) at R = 0.74 Å. The 1Σ_g singlet potential (S=0) supports about 330 bound and quasi-bound energy levels which correspond to different vibrational and rotational states. On the other hand, the 3Σ_u triplet potential (S=1) supports no bound states. Thus, if one could polarize all electronic spins of the atoms, then one would force all the colliding H atoms to interact via the triplet potential, thereby stabilizing the gas against recombination. Polarization is achieved experimentally by applying a large magnetic field. This technique is useful however only at very low temperatures since the Zeeman energy is very small.

The idea of spin-polarized hydrogen (denoted H+) has fascinated theorists for a long time, and this has resulted in a long series of papers on the subject. Some of the papers investigate the stability, others are about the thermodynamics of the gas. In this thesis, we are concerned with the former, but let us first go briefly over the latter, since the ultimate aim of our efforts in this area of low temperature physics is to study the thermodynamic properties of
a gas of H\(^+\) atoms.

An important theoretical prediction is that a gas of H\(^+\) will remain in the gaseous phase at all temperatures for pressures less than \(\approx 100\) bar (see Miller et al. 1977). Bose-Einstein condensation is also predicted for H\(^+\) (and T\(^+\)) in the bulk. The condition for 3-D Bose condensation for a weakly interacting Bose gas (which applies well to H\(^+\)) is (see Lifchitz et al. 1980):

\[
T_C = \frac{3.31 \pi^2}{mk_B} n_H^{2/3}
\]

where \(n_H\) is the density of H atoms and \(m\) is the mass of one hydrogen atom. For the highest reported densities, which are around \(1.5 \times 10^{16}\) cm\(^{-3}\) (Walraven 1980, Kleppner and Greytak 1980), the critical temperature would be \(T_C = 1\) mK, while for the lowest temperature at which experiments have been performed, namely \(T = 0.1\) K, the critical density would be \(n_H = 1.6 \times 10^{19}\) cm\(^{-3}\). Thus, the experimentalists are close to, but not yet at the point where they can observe Bose-condensation. The problem is, however, complicated by the presence of surfaces on which hydrogen binds, and it has been suggested that surface superfluidity can also take place even before 3D-condensation (see, for instance, Edwards and Mantz 1980).

The stability of spin-polarized hydrogen is still a hotly debated subject and, although H\(^+\) is clearly much more stable than unpolarized H, the extent of the improvement as a function of the magnetic field and temperature is not yet understood in detail. Calculations are difficult because recombination of hydrogen atoms into H\(_2\) molecules is intrinsically a three-body process:
\[ H + H + X \rightarrow H_2 + X, \] where \( X = \text{He}, \ H \) or wall. The third body is there only for conserving energy and momentum. In the early calculations, the recombination rate was predicted to have a field dependence \( R \propto e^{-\frac{\mu_e H_0}{k_B T}} \), where \( \mu_e \) is the magnetic moment of the electron and \( H_0 \) is the applied static magnetic field (see Jones et al. 1958). This implies a large decrease of the recombination rate with increasing \( \frac{H_0}{T} \). For instance, taking \( H_0 = 100 \text{ kG} \) (a conveniently achievable laboratory field) and \( T = 0.1^\circ \text{K}, \) we see that the rate is \( 10^{-60} \) times smaller than the rate with zero field. Such a field dependence is based on the assumption that the spin states will reach thermal equilibrium efficiently and rapidly. However, the strength of the relaxation mechanisms present, such as spin-exchange or dipole-dipole interactions, do not fully justify such an assumption since recombination itself disturbs the spin states from equilibrium.

More importantly, the situation is complicated by the fact that there is a coupling between the nuclear spin and the electronic spin which gives rise to a set of four spin states, the hyperfine states (Chapter Two) and which effectively prevents the achievement of complete electron spin polarization with available laboratory fields. It is now suspected that the recombination rate will rather go as \( R \propto \left(\frac{a}{2\mu_e H_0}\right)^2 \), where "a" is the coupling constant of the hyperfine interaction in the hydrogen atom. This means that we need to apply a very large field in order to improve significantly on the recombination rate, but that stabilization may still be feasible. However, there still remains the possibility of having \( R \propto R_0 + R_1(H) \), where \( R_0 \) is some constant independent of the field and where \( R_1(H) \)
goes to zero at high field. In such a case, there is no possibility of eliminating recombination although one can reduce the rate down to about $R_0$ by applying a strong magnetic field.

In this thesis, we shall investigate the field dependence of the recombination via $H + H + He \rightarrow H_2 + He$ which is dominant when a film of superfluid Helium is used to prevent binding to the walls at temperatures above 0.1°K. We shall restrict our investigation to the range of temperatures from 0.9°K to 1.3°K. The lower limit is imposed by practical considerations since temperatures below 0.9°K are not achievable in our experiment. The upper limit is due to the fact that the $^4$He vapor pressure increases rapidly with temperature, leading to a rapidly increasing recombination rate (Chapter Five).

The thesis will be organized as follows. In Chapter Two we shall give a brief review of the basic theory of the hydrogen atom, especially its hyperfine levels. Because magnetic resonance is used for detecting and studying the gas of hydrogen atoms, we shall describe this technique, and how it can be applied to the hydrogen atoms, in Chapter Three. In Chapter Four is listed a series of equations and concepts useful for understanding the signals. Chapter Five deals with the derivation of a simple model for recombination via $H + H + He \rightarrow H_2 + He$. Chapter Six contains information relevant to the experiment while Chapter Seven contains a description of the apparatus.
CHAPTER TWO

BASIC THEORY OF THE HYDROGEN ATOM

The hydrogen atom is a well known theoretical entity. In this chapter, information of interest to this work will be given and the notation used throughout the text will be introduced.

2-1. The Hamiltonian

The Hamiltonian of a single hydrogen atom consists of a part which depends on the position of both the proton ($\vec{R}$) and the electron ($\vec{r}$), and one spin dependent part. The former, denoted $H_o$, is the dominant one and the latter, denoted $H_s$, is handled perturbatively.

2-1-1. The Spatial Hamiltonian

This Hamiltonian gives the actual wave function of the hydrogen atom, denoted $\Gamma_i$, which obeys the following eigenfunction equation:

$$ H_o \Gamma_i(\vec{r}, \vec{R}) = E_i \Gamma_i(\vec{r}, \vec{R}) $$  \hspace{1cm} (2-1)

where $\vec{r}$ and $\vec{R}$ denote respectively the position of the electron and the proton, and $E_i$ is the energy of state $\Gamma_i$.

This wave function is derived in many textbooks on elementary quantum mechanics (see Laloe et al. 1977). Under the experimental conditions which we have, all atoms can be considered to be in their ground state, namely the 1s state. Therefore, $i = 1s$, and $\Gamma_i$ becomes:

$$ \Gamma_{1s} = \frac{1}{\sqrt{\pi a_o}} \frac{1}{3h^3} e^{\frac{i}{\hbar} \vec{P} \cdot \vec{R}} e^{-|\vec{R}-\vec{r}|/a_o} $$  \hspace{1cm} (2-2)
where $\vec{P}$ is the momentum of the proton, and $a_0$ the Bohr radius.

2-1-2. The Spin Hamiltonian

In the $1s$ state of the hydrogen atom, the fine structure term gives no correction, and only the contact term of the hyperfine Hamiltonian remains (as a second order correction term). If $\vec{M}_e$ and $\vec{M}_p$ are respectively the moment operators of the electron and the proton, then the expression of this Hamiltonian is:

$$H_{\text{h.f.}} = -A \vec{M}_e \cdot \vec{M}_p$$

(2-3)

where $A$ is just a constant to be given below. When a magnetic field, $\vec{H}$, is present, we have to add the term describing the coupling to this field:

$$H_C = -\vec{M}_e \cdot \vec{H} - \vec{M}_p \cdot \vec{H}$$

(2-4)

The moment operators can be rewritten in terms of the spin operators:

$$\vec{M}_e = \hbar \gamma_e \vec{S} \quad \text{and} \quad \vec{M}_p = \hbar \gamma_p \vec{I}$$

(2-5)

where $\gamma_e$ and $\gamma_p$ are the gyromagnetic ratio. In order to work with positive quantities, we use the convention that:

$$\hbar \gamma_e \equiv -\mu_e, \quad \hbar \gamma_p \equiv \mu_p \quad \text{and} \quad -A \hbar^2 \gamma_e \gamma_p \equiv a.$$  

(2-6)

That way, the total spin Hamiltonian becomes:

$$H_s \equiv H_{\text{h.f.}} + H_C = \mu_e \vec{S} \cdot \vec{H} - \mu_p \vec{I} \cdot \vec{H} + a\vec{I} \cdot \vec{S}$$

(2-7)
Note that the operators $\hat{S}$ and $\hat{I}$ are defined such that

\[
\hat{S} = \frac{1}{2} \hat{\sigma} \quad \text{and} \quad \hat{I} = \frac{1}{2} \hat{\tau}
\]

where $\hat{\sigma}$ and $\hat{\tau}$ are the usual Pauli matrices. The actual values of the constants are:

\[
\mu_e = -\hbar \gamma_e = 1.8570 \times 10^{-20} \text{ erg/Gauss}
\]

\[
\mu_p = -\hbar \gamma_p = 2.8213 \times 10^{-23} \text{ erg/Gauss}
\]

\[
a = -\Delta \hbar^2 \gamma_e \gamma_p = 9.4119 \times 10^{-18} \text{ erg.}
\]

The constant "a" and the ratio $\gamma_p / \gamma_e$ are known to a very high accuracy:

\[
\frac{a}{\hbar} = 1420.405 \, 751 \, 768 \, (2) \, \text{MHz} \quad \text{(Hellwig et al. 1970)}
\]

\[
\eta \equiv -\frac{\gamma_p}{\gamma_e} = 1.519 \, 270 \, 335 \, (15) \times 10^{-3} \quad \text{(Winkler et al. 1972)}
\]

or

\[
\frac{\hbar \gamma_p}{\mu_B} = 1.521 \, 032 \, 181 \, (15) \times 10^{-3} \quad \text{(idem)}
\]

where $\mu_B$ is the Bohr magneton.

Instead of using energy, one may want to use frequencies. The constants are then:

\[
\mu_e = 2.80247 \text{ MHz/Gauss}
\]

\[
\mu_p = 4.25771 \times 10^{-3} \text{ MHz/Gauss}
\]

\[
a = 1420.406 \text{ MHz}
\]
2-2. **Hyperfine Levels**

Consider a hydrogen atom in a static and uniform magnetic field along the z-axis: \( \hat{H} = H_0 \mathbf{k} \). Then the Hamiltonian (2-7) becomes:

\[
H_s = (\mu_e S_z - \mu_p I_z)H_0 + a\mathbf{I}\cdot\mathbf{S}
\]  

(2-11)

Our starting basis will be the one obtained by the direct product of the eigenstates of \( S_z \) and \( I_z \): \( |m_S, m_I>\), where \( m_S = \pm \frac{1}{2} \) and \( m_I = \pm \frac{1}{2} \). It is easily verified that \( |++> \) and \( |--\) are already eigenstates of \( H_s \). There remains a submatrix, mixing the other two states, which is easily diagonalized. The four eigenstates and their corresponding energies are given below in order of increasing energy:

\[
|1> = -\sin \theta |++> + \cos |--> 
\]

(2-12a)

\[
|2> = |-->
\]

b)

\[
|3> = \cos \theta |++> + \sin \theta |--> 
\]

c)

\[
|4> = |++>
\]

d)

where \( \tan 2\theta = \frac{a}{(\mu_e + \mu_p)H_0} \)  

(2-13)

\[
E_1 = -\frac{a}{4} - \frac{1}{2} \sqrt{a^2 + (\mu_e + \mu_p)^2H_0^2} 
\]

(2-14a)

\[
E_2 = \frac{a}{4} - (\mu_e - \mu_p) \frac{H_0}{2} 
\]

b)

\[
E_3 = -\frac{a}{4} + \frac{1}{2} \sqrt{a^2 + (\mu_e + \mu_p)^2H_0^2} 
\]

c)

\[
E_4 = \frac{a}{4} + (\mu_e - \mu_p) \frac{H_0}{2} 
\]

d)
2-3. The Hyperfine Levels at High and Low Fields

2-4-1. At Low Field

When the static magnetic field is very low, that is when 
\( H_0 \left( \mu_e + \mu_p \right)/a \ll 1 \), we see the three upper levels collapsing into the same level, while the bottom one stays apart. If we define \( \vec{F} = \vec{S} + \vec{I} \), then \( F \) and \( M_F \) are good quantum numbers in the low field limit.

Taking the limit \( H_0 \to 0 \) in equation (2-13), we obtain \( \cos \theta \to 1/\sqrt{2} \) and \( \sin \theta \to 1/\sqrt{2} \), so that the eigenstates (2-14) become:

\[
|1\rangle + \frac{1}{\sqrt{2}} |\leftrightarrow + \frac{1}{\sqrt{2}} |\leftrightarrow \equiv |0,0\rangle_F \tag{2-15a}
\]

\[
|2\rangle + |\leftrightarrow \equiv |1,-1\rangle_F \tag{b}
\]

\[
|3\rangle + \frac{1}{\sqrt{2}} |\leftrightarrow + \frac{1}{\sqrt{2}} |\leftrightarrow \equiv |1,0\rangle_F \tag{c}
\]

\[
|4\rangle + |\leftrightarrow \equiv |1,1\rangle_F \tag{d}
\]

where \( |\rangle_F \) refers to the coupled basis \( |F, M_F\rangle \). Taking the limit where \( H_0 \left( \mu_e + \mu_p \right)/a \) is very small, the expressions for \( E_3(H_0) \) and \( E_1(H_0) \) become:

\[
E_1 = -\frac{a}{4} \left[ 3 + \frac{(\mu_e + \mu_p)^2 H_0^2}{a^2} \right] \tag{2-16a}
\]

\[
E_3 = \frac{a}{4} \left[ 1 + \frac{(\mu_e + \mu_p)^2 H_0^2}{a^2} \right] \tag{b}
\]

While levels \( E_2 \) and \( E_4 \) are still given by expressions (2-14b,d).
2-4-2. At High Field

In the limit of high field, given by the condition $H_o (\mu + \mu_p)/a >> 1$, we obtain the almost decoupled basis:

$$|1> \rightarrow -\varepsilon |+> + |->$$  \hspace{1cm} (2-17a)

$$|3> \rightarrow |+> + \varepsilon |->$$  \hspace{1cm} (2-17b)

Since $\cos \theta \rightarrow 1$ and $\sin \theta \rightarrow \frac{a}{2H_o(\mu + \mu_p)} \equiv \varepsilon$ (2-18)

where $\varepsilon$ is called the admixture coefficient. The corresponding energies are:

$$E_1 = -\frac{a}{4} - \frac{(\mu + \mu_p)H_o}{2}$$  \hspace{1cm} (2-19a)

$$E_3 = -\frac{a}{4} + \frac{(\mu + \mu_p)H_o}{2}$$  \hspace{1cm} (2-19b)

Note that states $|2>$ and $|4>$ are independent of field and their energies are given by (2-14b,d) for all fields.
Figure 2-1: Energy of the hyperfine states as a function of the field.
CHAPTER THREE

MAGNETIC RESONANCE OF HYDROGEN

Magnetic resonance is a particularly useful technique for studying H-atoms because the magnetic resonance spectrum of hydrogen is quite distinctive. As we saw in Chapter Two, the hydrogen atom has four hyperfine levels in its ground state, and it would be a formidable task to solve analytically the equations giving the time evolution of this system when a time dependent magnetic field is applied. However, the hyperfine levels are very sharp, and if none of the six energy differences are very close to each other, then we can assume that we are looking at only two levels when the atoms are excited with an RF magnetic field. In other words, the RF field couples effectively only two levels and, as far as magnetic resonance is concerned, it is a two-level system.

Since the motion of a spin-$\frac{1}{2}$ in a magnetic field is described in all textbooks on magnetic resonance, we shall take a more general approach here. Starting with the definition of a general two-level system (for which a spin-$\frac{1}{2}$ is just a special case), we shall find its equation of motion and show that it can be rewritten in a form similar to that of a real spin-$\frac{1}{2}$. Then we will discuss the technique of pulsed magnetic resonance.

3-1. General Two-Level System

Consider a quantum system possessing two, or more, energy levels which are eigenstates of some Hamiltonian, $H$. We shall say that we have a two-level system if there exists a second
(time-dependent) Hamiltonian, $H'$, which couples only one pair of levels together. We shall assume that these two levels are non-degenerate and $H'$ possesses only non-diagonal elements in the subspace of these two levels. If these two levels are denoted $a$ and $b$, for which the energies are $E_a$ and $E_b$, and if the system is in state $\psi$, then we can define the density matrix as (see Merzbacher 1970):

$$
\rho = \begin{pmatrix}
\rho_{aa} & \rho_{ab} \\
\rho_{ba} & \rho_{bb}
\end{pmatrix} = \begin{pmatrix}
\rho_{aa} & \rho_{ab} \\
\rho_{ab}^* & 1-\rho_{aa}
\end{pmatrix}
$$

(3-1)

where $\rho_{ij} = \langle i|\psi\rangle\langle\psi|j \rangle$ for $i,j = a,b$. Consider now a matrix operator $\hat{O}$, and the matrix operator $\hat{S} = \frac{1}{2} \sigma$ which was introduced in Chapter Two. Because it is a two by two matrix, we can rewrite $\hat{O}$ as:

$$
\hat{O} = A_0 + 2\vec{A} \cdot \hat{S}
$$

(3-2)

where $A_0 \equiv \frac{1}{2} \text{Tr}(\hat{O})$ and $\vec{A} \equiv \text{Tr}(\hat{O}\hat{S})$.

(3-3)

For instance, if $\hat{O}$ is the total Hamiltonian $H_{\text{tot}} = H + H'$, then:

$$
H_{\text{tot}} = h_0 + 2\hat{h} \cdot \hat{S}
$$

(3-4)

where $h_0 \equiv \frac{1}{2} \text{Tr}(H) \equiv \bar{E}$ and $\hat{h} \equiv \text{Tr}(H'\hat{S})$.

Suppose now that $\hat{O} = \rho$, then a similar procedure gives:

$$
\rho = \frac{1}{2} + 2<\hat{S}> \cdot \hat{S}
$$

(3-5)

where $<\hat{S}> = \text{Tr}(\rho\hat{S})$ is now the expectation of the operator $\hat{S}$. It comes in fact from the definition of the density matrix that, for any operator $\hat{O}$, the expectation value is given by:
$$\langle \hat{\mathbf{S}} \rangle \equiv \text{Tr}(\hat{\rho} \hat{\mathbf{S}}) \quad (3-6)$$

It is a useful fact that the density matrix can be rewritten in terms of \( \langle \hat{\mathbf{S}} \rangle \), a vector, which will now characterize the system. We shall denote \( S_x, S_y \), and \( S_z \) the components of \( \hat{\mathbf{S}} \) in the fictitious space, corresponding respectively to \( S_x, S_y \), and \( S_z \). Physically, \( \langle S_x \rangle \) and \( \langle S_y \rangle \) are a measure of the correlation between the states, while \( \langle S_z \rangle \) is a measure of the energy. \( \langle H \rangle \) is given by:

$$\langle H \rangle = \frac{E_a + E_b}{2} + \langle S_z \rangle (E_a - E_b)$$

or

$$\langle \Delta H \rangle \equiv \langle H \rangle - \bar{E} = \langle S_z \rangle \Delta E$$

(3-7)

where \( \Delta E \equiv E_a - E_b \) and \( \bar{E} \equiv (E_a + E_b)/2 \).

When more than one system are under consideration, say \( N \), and if they are weakly interacting, then we can just use the average density matrix which is defined as:

$$\bar{\rho} \equiv \frac{1}{N} \sum_{i=1}^{N} \rho_i$$

(3-8)

Thus, instead of (3-5) we have:

$$\bar{\rho} = \frac{1}{2} + 2 \langle \hat{\mathbf{S}} \rangle_T \cdot \hat{\mathbf{S}}$$

(3-9)

where the subscript \( T \) specifies the "thermal" average, i.e. we use \( \bar{\rho} \) rather than \( \rho \).

We can now make the analogy between a spin-1/2 and our general two-level system. As mentioned in Chapter Two, the Hamiltonian of
a spin-$\frac{1}{2}$ in a magnetic field is: $H = -\mathbf{H} \cdot \mathbf{H} = -\mu \mathbf{S} \cdot \mathbf{H}$. We then see that (3-4) has this form if we put:

$$2\hbar = -\mu \mathbf{H}',$$

(3-10)

(see Abragam 1961, p. 36), where the prime specifies that both $\mu'$ and $\mathbf{H}'$ now refer to a fictitious spin for which the operator is $\hat{\mathbf{S}}$. The analogy can be visualized more clearly by substituting equation (3-4) into the Schrödinger equation for density matrices, namely:

$$\frac{d\rho}{dt} = -\frac{i}{\hbar} [H_{\text{tot}}, \rho]$$

(3-11)

We then obtain:

$$\frac{d\langle \hat{S} \rangle}{dt} = \frac{2\hbar \times \langle \hat{S} \rangle}{\hbar} = -\frac{\mu \mathbf{H}}{\hbar} \times \langle \hat{S} \rangle$$

(3-12)

which is exactly the equation of motion of a spin-$\frac{1}{2}$ in a magnetic field (see Slichter 1978).

This yields a set of three coupled equations giving the evolution of a spin-like system when no relaxation mechanisms are present. Note that the term $h_o$, the average energy of the two levels, has no effect on the evolution of the system, and that $\hbar$ may well be time dependent. Naturally, the system tends toward equilibrium conditions, due to relaxation mechanisms. In the usual treatment of Magnetic Resonance, one introduces empirical relaxation terms in the equation of evolution of the spins in such a way that we obtain two relaxation times $T_1$ and $T_2$. $T_1$ is the "spin-lattice" relaxation time for the component of $\mathbf{S}$ along the static field, $\mathbf{H}_o$, usually $S_z$. $T_2$ is the
"spin-spin" relaxation time and belongs to the components of \( \hat{S} \) in the plane normal to \( \hat{H}_o \). The resulting equations are known as the "Bloch equations":

\[
\begin{align*}
\frac{d< S >}{dt} &= -\mu' \langle \hat{H}' \times \hat{S} \rangle \gamma + \frac{S -< S >}{T_1} \\
\frac{d< S >}{dt} &= -\mu' \langle \hat{H}' \times \hat{S} \rangle \beta - \frac{\beta}{T_2} \\
\frac{d< S >}{dt} &= -\mu' \langle \hat{H}' \times \hat{S} \rangle \alpha - \frac{\alpha}{T_2}
\end{align*}
\] (3-13a)

where \( S_o \) is the equilibrium value for \( \hat{S} \) in the static field.

We can derive the relaxation terms from the knowledge of the system at the microscopic level. Consider the following equation:

\[
\frac{d\rho}{dt} = \begin{pmatrix} (\rho_o^{aa} - \rho_{aa})/T_1 & -\rho_{ab}/T_2 \\ -\rho_{ba}/T_2 & (\rho_o^{bb} - \rho_{bb})/T_1 \end{pmatrix}
\] (3-14)

Using equation (3-5), this becomes:

\[
\begin{align*}
\frac{d}{dt} \begin{pmatrix} < S > \\ < S > \\ < S > \end{pmatrix} &= \begin{pmatrix} < S > \\ < S > \end{pmatrix} \\
&= \begin{pmatrix} < S >_{\gamma} -< S >_{\gamma} \\ -< S >_{\gamma} +< S >_{\gamma} \\
&\frac{< S >_{\gamma} -< S >_{\gamma}}{T_1} -\frac{-< S >_{\gamma} +< S >_{\gamma}}{T_2} \end{pmatrix}
\end{align*}
\] (3-15)

or

\[
\frac{< S >}{T_1} = -\frac{< S >}{T_2}
\]

where \( S_{\pm} = S_{\alpha} \pm iS_{\beta} \). These two expressions are merely the relaxation terms of the Bloch equations.
We then see that the actual calculation of the relaxation times, $T_1$ and $T_2$, is a microscopic quantum mechanical problem.

3-2. Case of the Hydrogen Atom

In our experiment, the exciting field, $H_1 \cos \omega t$, is applied at right angle to the static magnetic field, say the $x$-axis, so that the interaction Hamiltonian, $H'$, will become (using equations (2-4), (2-5) and (2-6)):

$$H' = (\mu^S_x - \mu L)H_1 \cos \omega t = -\mu S_x H_1 \cos \omega t$$  \hspace{1cm} (3-16)

Consider now a pair of hyperfine states (see Chapter Two) of the hydrogen atom: $|a\rangle$ and $|b\rangle$. In this basis, $H'$ has no diagonal elements for any pair of hyperfine states, and, since $<a|M_x|b>$ = $<b|M_x|a>$, the interaction Hamiltonian is proportional to $S_\alpha$, the equivalent of $S_x$ in this fictitious space. From (3-10) and (3-4), we then obtain:

$$-\mu'\hat{H} = 2\text{Tr}(H'\hat{S})$$
$$= -2<a|M_x|b>H_1 \cos \omega t \hat{\alpha}$$  \hspace{1cm} (3-17)

It is then legitimate to define:

$$\mu' \equiv 2<a|M_x|b> = \mu^{ab}$$  \hspace{1cm} (3-18)

The hydrogen atom will consequently behave like a spin-$\frac{1}{2}$ of gyromagnetic ratio $\mu^{ab}$ excited by a field $H_1 \cos \omega t$. 
Pulsed Magnetic Resonance

Pulsed MR proceeds in two steps. One first irradiates the sample (which sits in a static homogeneous magnetic field) with a time dependent magnetic field, $H(t)$, for a period of time, $\tau$, which is sufficiently short that the system does not have enough time to relax. Second, the exciting field is turned off and the system can evolve according to its own Hamiltonian. A cavity tuned at the appropriate frequency is used as a probe for exciting the system during the time $\tau$, and for detecting the resultant signal which is due to the fluctuating magnetic moment of the sample. This cavity is part of our detection device, which also includes a transmission line and a spectrometer. This spectrometer is thoroughly described in Lorne Whitehead's thesis (Whitehead 1979). The cavity will be described in Chapter Seven.

We are interested in the solution of the Bloch equations in both regimes of pulsed MR. We will only quote the results here, since they are derived in most textbooks on magnetic resonance (Slichter 1978). Suppose that we start from the equilibrium condition: $\langle S(0) \rangle = (0,0,S_0)$, i.e. no correlations and a fully relaxed system, then the evolution of the system during the pulse is given by the following equations if the pulse is very short:

\[
\begin{align*}
\langle S_\gamma \rangle(t) &= S_0 \cos(\omega_1 t) \\
\langle S_\beta \rangle(t) &= S_0 \sin(\omega_1 t) \sin(\omega_0 t) \\
\langle S_\alpha \rangle(t) &= -S_0 \sin(\omega_1 t) \cos(\omega_0 t)
\end{align*}
\]
where \( \omega_1 \equiv \frac{\mu^1 H_1}{2\pi} \) and \( \omega_0 \equiv \frac{\mu^0 H_0}{\pi} \).

Normally, we will apply what are called "\( \frac{\pi}{2} \)-pulses" which bring \( <\hat{S}> \) from the \( \gamma \)-axis down into the \( \alpha-\beta \) plane. From equations (3-19), we see that this requires that:

\[
\omega_1 \tau = \frac{\pi}{2}
\]

(3-20)

Following such a pulse, the evolution of the system is given by:

\[
<S^\gamma>(t) = S_0 (1-e^{-t/T_1})
\]

(3-21a)

\[
<S_\beta>(t) = -S_0 e^{-t/T_2} \cos \omega_0 t
\]

b)

\[
<S_\alpha>(t) = S_0 e^{-t/T_2} \sin \omega_0 t
\]

c)

This is the basic scheme in pulsed MR, but there exist others which have special purposes. "Spin echo" is one of them, and one version of it consists in the application of a \( \pi/2 \) pulse, followed after a time \( T \) by a \( \pi \)-pulse (=\( 2\pi/2 \)). An echo signal will appear at \( t = 2T \), the amplitude of which is given by \( S_0 e^{-2T/T_2} \) (Slichter 1978, p. 42). This is a useful scheme for measuring \( T_2 \) when the magnet has a poor homogeneity which results in short decay times (see Chapter Four).
CHAPTER FOUR

SIGNAL THEORY AND LEVEL DYNAMICS

The signal to be detected is expected to be very weak, compelling us to a very careful identification and estimate of all the parameters involved. We need to understand the effects of the resonator, which is one of the key parts of the detection system, and to know the expected strength of the signal.

4-1. Principle of the Resonator

The resonator which we use is designed to detect the oscillating magnetic moment produced by the spin ensemble under study.

Since we have a fluctuating magnetic moment, energy can be transferred to the resonator. Let $P_S$ be the power delivered to the resonator by the spins. We have ohmic power loss in the resonator, $P_R$, and power $P_L$ flowing in the transmission line to the spectrometer. At steady state, we must have $P_S = P_R + P_L$. At critical coupling, we have $P_L = P_R$.

Now, in a quite general way, the quality factor, $Q$, of any resonator is given by the expression:

$$ Q = \frac{\text{Stored Energy}}{\text{mean power loss}} = \frac{\omega U}{<P_R>} \quad (4-1) $$

where $\omega$ is the angular frequency, $U$ the stored energy and $<P_R>$ the mean power loss per cycle. These quantities can in principle be calculated, but any level of accuracy requires a careful measurement of $Q$. 
Defining $H_1(0)$ as the value of the amplitude of the oscillating magnetic field at $r = 0$, the "centre" of the resonator, we obtain:

$$U = \beta H_1^2(0) \quad (4-2)$$

where $\beta$ is a normalized field energy factor, which has units of volume. Its exact expression is:

$$\beta = \frac{\int d^3r}{V_R} \frac{H_1^2(r)}{H_1^2(0)} \quad (4-3)$$

For a homogeneous field filling the volume $V_R$ of the resonator it reduces to:

$$\beta = \frac{V_R}{8\pi} \quad (4-4)$$

On the other hand, we can write:

$$<P_R> = \frac{\gamma}{\sigma \delta} H_1^2 \quad (4-5)$$

where $\sigma$ is the conductivity of the metal, $\delta$ the skin depth and $\gamma$ some geometrical factor having the following analytical expression (see Jackson 1975):

$$\gamma = \frac{c^2}{32\pi^2} \int_{S_R} \text{d}a \left| \vec{n} \times \vec{H}_n \right|^2 \quad (4-6)$$

where $\vec{n}$ is the normal to the surface, $\vec{H}_n$ the magnetic field parallel to the surface and $S_R$ the total surface.

Thence the expression (4-1) becomes:

$$Q = \frac{\beta}{\gamma} \delta \sigma \omega \quad (4-7)$$
where the skin depth, \( \delta \), is given by:

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

(4-8)

Therefore, for a given resonator with ohmic losses at the metal surfaces, \( Q \) takes the form:

\[
Q = A(\omega_0)^{\frac{1}{2}}
\]  

(4-9)

where \( A \) is a constant of the resonator.

Our aim, here, is not only to find expressions which give us a good understanding of the resonator, but also to relate the field in the resonator to whatever we can measure from the outside.

Equation (4-5) can be rewritten as:

\[
H_1 = \left( \frac{\sigma \delta \langle P_R \rangle}{\gamma} \right)^{\frac{1}{2}}
\]  

(4-10)

Since, at critical coupling \( Q = Q_c, P_R = P_L \), and \( P_S = P_R + P_L \), we can furthermore write (4-10) as:

\[
H_1 = \left( \frac{\sigma \delta \langle P_S \rangle}{2\gamma} \right)^{\frac{1}{2}}
\]  

(4-11)

Finally, using equation (4-7), we get:

\[
H_1 = \left( \frac{Q \langle P_S \rangle}{2\beta \omega} \right)^{\frac{1}{2}} = \left( \frac{Q \langle P_L \rangle}{\beta \omega} \right)^{\frac{1}{2}}
\]  

(4-12)

4-2. Spin Ensemble and Strength of the Signal

As mentioned previously, the resonator is merely a probe for magnetic moments which result from the total contribution of all "spins" in the sample. On the other hand, every spin feels the
local field and responds to it.

So, in general, the power involved when spins evolve in a magnetic field is given by:

\[ <P_S> = \int_{V_R} <\hat{M} \cdot \hat{B}> t \, d^3r \]  

(4-13)

where \( \hat{B} = \hat{H} + 4\pi \hat{M} \),

(4-14)

and \( < >_t \) means time averaging. Assume first that \( \hat{H} = \hat{H}_1 \cos(\omega t + \phi_1) \hat{i} \) is the field produced by the sample and that it is uniform throughout the resonator and the sample, which occupies a finite volume \( V_S \). If every moment, \( \hat{u} \), precesses around the static and locally homogeneous field \( \hat{H}_0 = \hat{H}_0 \hat{k} \), and if the density of the spins is \( \rho_S \), then:

\[ \mu_x = \mu \sin \omega t \]  

(4-15)

\[ M_x = \rho_S \mu_x \]  

(4-16)

Hence, the power \( <P_S> \) which we can detect will be:

\[ <P_S> = \int_{V_R} \frac{d}{dt} (\rho_S \mu \sin \omega t) \cdot (\hat{H}_1 \cos(\omega t + \phi_1) + 4\pi \rho_S \mu \sin \omega t) \, d^3r \]

\[ = \frac{N\mu}{2} \left( \frac{V_S}{V_R} \right) \omega H_1 \cos \phi_1 \]  

(4-17)

where \( N \) is the total number of spins. At resonance, \( \phi_1 \) goes to zero, and, defining \( N\mu \equiv m \) and \( V_S/V_R \equiv n \), the filling factor, equation (4-17) becomes:

\[ <P_S> = n \frac{m}{2} \omega H_1 \]  

(4-18)
we can now combine this expression with equation (4-12) and obtain a relationship between the moment of the spins and their power output:

\[ <P_L> = \eta^2 \frac{m^2 \omega Q}{16\beta} \]  

(4-19)

Because we assumed homogeneity, the factor \( \beta \) is merely equal to \( V_R/8\pi \) and we finally get:

\[ <P_L> = \frac{\pi\eta^2 m^2 \omega Q}{2V_R} \]  

(4-20)

Obviously, this describes an ideal resonator and the equations have to be generalized to a more realistic case. We shall not go into that here, but we shall mention that (4-20) does not change very much, and that the calculation of \( \eta \) would require an accurate knowledge of the magnetic field (see Bloembergen and Pound 1954).

4-3. Multilevel Dynamics

We use a resonator to probe the spin, or moment, ensemble which is our sample. Each of these small moments is in fact one hydrogen atom, and each atom has some calculable effective magnetic moment which depends on the static magnetic field, \( H_0 \), and on which set of two levels we are looking at.

The strength of the signal, which we detect, is closely related to the population of these two levels, and the population distribution is itself governed by the dynamics of these levels, which, in turn, can be affected by the probing resonator.

The dynamics is given by a series of mechanisms which can be split into two broad classes: Relaxation mechanisms and recombination
mechanisms. In the first class we put those mechanisms which do not alter the total population of the atoms directly. These mechanisms are more or less standard in magnetic resonance. Because the total population is time-dependent, we have to consider relaxation due to the recombination of atoms into molecules, which we shall therefore put in a separate class.

It is worth noticing that this list is not exhaustive, and some mechanisms, such as "pressure shift", will not be discussed because they are not important for the present experiments.

4-3-1. Relaxation Mechanisms

Following a π/2-pulse, the signal starts at some amplitude and then decays. We can obtain some information on the relaxation mechanisms involved by studying this decay. Nevertheless, some undesirable mechanisms will modify, or quench, those mechanisms in which we are interested. In the following, we shall first describe the unwanted mechanisms which we think will be the most important. Spin exchange, which is the main mechanism under study, will then be described.

(i) Inhomogeneity of the Static Field

When the static magnetic field is inhomogeneous, the precessing spins lose their correlation and they get out of phase, resulting in a superimposed $T_2$ mechanism. The corresponding $T_2$ is given by (see Abragam 1961, p. 50):

$$T_2^* = \frac{1}{\Delta \omega}$$  \hfill (4-21)
where the star indicates that it is not a real relaxation mechanism.  

\[ \Delta \omega = 2 \pi \Delta f \] is the spread in frequency due to inhomogeneity as it is calculated in Chapter Six. Over the volume of our sample, which is about 1.5 cm\(^3\), the magnet used has a homogeneity \( \Delta H/H \approx 10^{-6} \) at 42 kG (and this is expected to be improved by the new set of shim coils, see Appendix A). As we shall also see in Chapter Six, two fields, corresponding to two transitions, are of interest to us, and scaling down the above inhomogeneity, we obtain from equations (6-4), (6-5) and (4-21) that:  

\[ T_2^* (405 G) = 1.6 \times 10^{-4} \text{ sec.} \]  
\[ T_2^* (6.5 kG) = 3.2 \times 10^3 \text{ sec.} \]  

Although the magnetic moment at 405 G is about twenty times larger than at 6.5 kG, the homogeneity of the magnet is much more important, and may easily make the signal difficult to see. If the atoms did not move in the inhomogeneous field then the signal might still be recovered by the spin-echo technique. However, this is not possible because the atoms in the sample diffuse rapidly.

(ii) Diffusion

The 'sample' consists of a closed tube filled with a mixture of hydrogen and helium gas. Therefore, atoms will diffuse, especially at very low temperatures (\(\approx 1 \text{ K}\)) where the \(^4\text{He}\) density, \(n_{\text{He}}\), drops drastically. Following a \(\pi/2\)-pulse, the movement of the atoms will destroy the correlation among the phases if the field is not homogeneous.

Calculations of the effect of diffusion on the shape of the signal are given by Carr and Purcell (Carr and Purcell 1954). Considering a simple gradient in \(H_z\), they found that the induced decay will be of the form:
\[ M(t) = M_0 \exp \left\{ -\mu^2 \left( \frac{\partial H}{\partial z} \right)^2 \frac{2Dt^3}{3} \right\} \] (4-22)

where \( D \) is the diffusion constant. This shape, which is superimposed on the usual exponential decay, resembles a Gaussian shape.

Measurements were done on the diffusion constant for the diffusion of hydrogen atoms in helium gas near 1°K (see Hardy et al. 1980). Using the relation:

\[ D = \left( \frac{3\pi}{32} \right) \frac{\bar{v}}{Q_{\text{He}}} \] (4-23)

where \( \bar{v} \) is a thermally averaged relative speed of H-He pair and \( Q \) is the thermally averaged diffusion cross-section, they found that \( Q = 20 \pm 1 \) \( ^\circ \text{K} \) for a temperature range \( 0.98 < T < 1.24 ^\circ \text{K} \). This is an important number in this experiment.

(iii) Radiation Damping

As the reradiating atoms excite the resonator, the consequences of Joule heating can damp the very weak signal which is being emitted. Surprisingly, a high \( Q \) resonator will damp the signal more than a low \( Q \) one, although it offers less ohmic losses. In fact radiation damping comes from the influence of the radiated field on the sample itself (Bloom 1957). This was the main decay mechanism in the zero field experiment, and the \( Q \) of the resonator had to be reduced for certain of the experiments (Hardy et al. 1980). In our experiment, it is possible to face similar problems, thereby requiring some knowledge of the effect of radiation damping on the signal.
We shall concentrate on the major consequence of radiation damping, namely the short-circuiting of the intrinsic $T_2$-mechanisms of the sample. If $Q$ is the quality factor of the resonator, $\eta$ the filling factor, $\mu$ the "effective" magnetic moment and $M(0)$ the initial magnetization of the sample, then the characteristic time for radiation damping is approximately given by:

$$\tau \approx \frac{1}{2\pi Q\eta\mu M(0)}$$

(4-24)

In Chapter six, it will be demonstrated that $M(0) = n\mu(P_j - P_i)$ where $n$ is the atom density and $P_j - P_i$ is the population difference. Therefore equation (4-24) becomes:

$$\tau \approx \frac{h}{Q\eta\nu^2(P_j - P_i)}$$

(4-25)

In our experiment, there are two possible transitions for which the $\mu$'s are: $\mu^{23} = 7.53 \times 10^{-20}$ erg/Gauss (at 6.5 kG) and $\mu^{23} = 1.67 \times 10^{-22}$ erg/Gauss (at 405 G). If we assume $Q = 1000$, $\eta = 0.1$, $T = 1^\circ K$ and $n = 5 \times 10^{12}$ cm$^{-3}$, then we obtain:

$$\tau(405\text{G}) \approx 5.2 \text{ sec}$$

$$\tau(6.5\text{kG}) \approx 1.8 \times 10^3 \text{ sec}$$

Radiation damping is clearly not important at 6.5 kG, and, even if it is much smaller at 405 G, the homogeneity problem will dominate. Note that radiation damping is much more important for the zero field experiments because $\mu$ is much larger.
(iv) **Spin Exchange**

Intrinsically, a gas of hydrogen atoms possesses relaxation mechanisms. The two most important ones are spin-exchange and dipole-dipole interactions. Although the latter is a rather weak process, it will dominate when spin-exchange becomes ineffective (Statt and Berlinsky). Theoretical calculations have been done for both processes and we shall only quote the main results since they will be discussed further in Chapter Five in the context of the recombination problem. We shall start with spin-exchange.

According to Berlinsky and Shizgal (Berlinsky and Shizgal 1980), all spin-exchange transition rates can be written in terms of three quantities: two temperature-dependent cross-sections, \( \sigma^+ \) and \( \sigma^- \), each referring to a sum over even (+) and odd (-) angular momentum states, and one field dependent factor, \( X = \sin^2 2\theta \), \( \theta \) being the angle defined in Chapter Two. At low temperatures \( \langle \sigma^- \rangle_T \) becomes negligibly small whereas \( \langle \sigma^+ \rangle_T \) reaches some limit around 1 A^2. It is found that, at all temperatures and fields, level 2 and 4 have same rate: \( \dot{p}_2 = \dot{p}_4 \), where \( p \) is the population of the level. Then, spin-exchange does not relax the difference of populations of the Zeeman states. Moreover, spin-exchange cannot cause transitions within the manifold of states 1 and 2. This means that no transition between levels 1 and 2 will take place if the colliding atoms are in a combination of states 1 and/or 2. This is a strong selection rule which says that there will be no equilibration of these two levels if the other two hyperfine states (3 and 4) are not populated. This happens for high magnetic fields and low temperatures.

Finally, we can mention that, if we define the relaxation time \( T_1 \) as the
rate at which \( p_3 \cdot p_1 \) relaxes, then we can relate the \( T_1 \)'s at all fields by:

\[
\frac{1}{T_1(H)} = \frac{X}{T_1(0)} \tag{4-26}
\]

It is interesting to look at some numbers. For a density \( n = 5 \times 10^{13} \text{ cm}^{-3} \) and a temperature \( T = 4.2^\circ K \) it was measured that \( T^{-1} = 72 \text{ sec}^{-1} \) (Berlinsky et al. 1980), all in zero field. Extrapolating the calculations of Berlinsky et al. to \( T = 1^\circ K \) and \( n = 5 \times 10^{12} \text{ cm}^{-3} \), which is more in our range of interest, we obtain \( T_1^{-1} = 5.8 \text{ sec}^{-1} \), or \( T_1 = 0.17 \text{ sec} \). As the magnetic field is increased, \( X \) decreases, thereby increasing \( T_1 \). For \( H = 6.5 \text{ kG} \), \( T_1 \) will be \( T_1 = 28 \text{ sec} \). Thus, we are working with very long spin lattice relaxation times, and this will hamper the usage of signal averaging, which is a useful tool for detecting weak signals.

(v) **Dipole-Dipole Interactions**

Assuming that only levels 1 and 2 were significantly populated, Statt and Berlinsky (Statt and Berlinsky) calculated \( T_1 \) due to dipole-dipole interactions in high magnetic field. They found that

\[
T_1^{-1} = n_H \left[ 1 + \varepsilon \frac{\gamma_e}{\gamma_p} \right] A,
\]

where \( \varepsilon \) is the admixture coefficient defined in Chapter Two and \( A \) is a factor independent of \( n_H \) or \( \varepsilon \). Using this relation, we can extrapolate their equation (10) which was calculated for \( H_o = 100 \text{ kG} \) and \( n_H = 10^{16} \text{ cm}^{-3} \), and we obtain:

\[
T_1^{-1} \approx n_H \left[ 1 + \varepsilon \frac{\gamma_e}{\gamma_p} \right] (6.79T^{1/2} - 0.746T^{2/3}) \cdot 10^{-20} \text{ sec}^{-1} \tag{4-27}
\]
Consider a density of $5 \times 10^{12} \text{ cm}^{-3}$, a field $H = 6.5 \text{ kG}$ and a temperature $T = 1^\circ \text{K}$, then equation (4-29) yields:

$$T_1^{-1} = 2.14 \times 10^{-14} \text{ s}^{-1} \text{ or } T_1 = 4670 \text{ sec}.$$ 

We can then conclude that dipole-dipole interactions will be important in our experiment only if the density increases considerably.

4-3-2. **Recombination**

There exist many routes for the recombination of hydrogen atoms into a hydrogen molecule. In all cases, a third body is required for conserving energy and momentum. Depending on the experimental conditions, certain schemes will dominate. In this experiment, recombination in the bulk by the process $\text{H} + \text{H} + \text{He} + \text{He} \rightarrow 6 \text{ } _{1}^{2} \text{H} + \text{He}$ will dominate, since the helium density is about $10^{-10}$ times larger than the hydrogen density and since the binding to the wall is negligible in the range of temperatures achievable with our apparatus.

A model for recombination will be described in the next chapter. The most important feature of this model is that recombination depends on the hyperfine states of the colliding atoms, and, consequently, the recombination rate will depend on the population distribution of the atoms among the hyperfine states. An extreme case would be a gas of hydrogen atoms all in the $h = 2$ hyperfine state. In that case, there will be no recombination at all and the gas will be stable (if we neglect spin-spin interactions and wall effects).

Hence, relaxation mechanisms and recombination are deeply interconnected and the dynamics of the hyperfine levels is the result of both of them. For this reason, the model derived in the next
chapter will include spin-exchange as the relaxation mechanism.
Bulk recombination involving the process $H + H + He \rightarrow H_2 + He$ will be considered in this chapter and a simple model will be derived.

5-1. Preliminaries

The process $H + H + He \rightarrow H_2 + He$ has been investigated experimentally in zero field, and for temperatures ranging from about 1°K to 1.25°K, (Hardy et al. 1980). A simple model was used to explain the data. When no explicit consideration is taken of the hyperfine structure of the hydrogen atoms, we can regard the recombination problem as a chemical process where the reacting particles have some probability of colliding together and reacting. This leads to a rate equation of the type:

$$\dot{n}_H = -k n_{He} n_H^2$$

where $n_H$ and $n_{He}$ are respectively the hydrogen atom and helium atom densities. The factor $k$ is just a measure of the efficiency of the collision. An exact solution can be found to this equation, and it is:

$$n_H(t) = \frac{n_H(0)}{1 + t/t_R}$$

where we define $t_R^{-1} = k n_{He} n_H(0)$. Note that in this model, the characteristic time, $t_R$, depends on the initial densities.
Although elementary, this model succeeded in explaining the data. Indeed, by plotting $\frac{d(1/n_H)}{dt}$ against $n_{\text{He}}$ (which is directly related to the temperature), we obtain a straight line whose slope is $k$. The average $k$ obtained is:

$$k = (0.28 \pm 0.03) \times 10^{-32} \text{ cm}^6 \text{s}^{-1}.$$ 

This simple model makes no prediction about the field dependence of the recombination. In order to find the effect of a field, we have to include the spin degrees of freedom in the problem since the interaction between hydrogen atoms depends on the hyperfine state of the atoms. Obviously, then, the recombination rate will depend on the population distribution among the hyperfine states and, consequently, the relaxation mechanisms will play a crucial role in the recombination problem. Therefore, any realistic model for recombination includes relaxation mechanisms.

As mentioned in Chapter Four, spin-exchange is the dominant relaxation mechanism in low field ($6.5$ kG is considered small when the temperature is around $1^\circ$K since $\mu_e H < kT$). We shall therefore take spin-exchange for the relaxation of the hyperfine states in our model. The strategy will then be to derive the model for the recombination rate and thereafter to include the equations describing spin-exchange (Berlinsky 1979). Finally, the parameters will be matched to the existing data.

5-2. Asymptotic States

In a scattering problem, the usual approach is to look at the asymptotic wave functions of the colliders, far from the scattering
site. In that limit, the atoms are free and the total wave function is given by the direct product of the respective wave functions, or states. In our problem, three atoms come in (two hydrogen atoms and a helium atom) and one molecule plus one atom come out (a hydrogen molecule and the helium atom).

The helium atom is there only for conserving energy and momentum. \(^{4}\text{He}\) behaves like a neutral body since it has a total electronic spin equal to zero (\(S=0\)) and has zero nuclear spin (\(I=0\)). Hence, the spin part does not enter directly into the scattering problem, so that the asymptotic helium state can be denoted simply by:

\[
|\text{He}\rangle = |p_3^> \tag{5-3}
\]

where \(p_3\) is the momentum.

The hydrogen molecule resulting from the collision has, obviously, \(S = M_S = 0\), and can be in any of its vibrational (\(v\)), rotational (\(\ell\)) and nuclear spin (\(I, M_I\)) states. The asymptotic state is then:

\[
|H_2\rangle = |v, \ell, I, M_I, \hat{k}\rangle \tag{5-4}
\]

where \(\hat{k}\) is the momentum. However, \(I + \ell\) must be even.

The case of the hydrogen atoms is somewhat more complicated because, first, the nuclear and electronic spins are coupled by the hyperfine interaction (see Chapter Two) and, second, these two particles are identical, requiring an antisymmetrized state. The interaction between two hydrogen atoms depends on their total electronic spin, \(S\) (see Chapter One). Thus we have to relate the hyperfine states to the simply-coupled basis: \(|S_M_S, I_M_I\rangle\). This
A relationship is easily found and is formally written as:

\[ |h_1, h_2> = \sum_{SM_S} \sum_{IM_I} A(h_1, h_2; IM_I, SM_S) |SM_S, IM_I> \] (5-5)

where \( A(h_1, h_2; IM_I, SM_S) \equiv <SM_S, IM_I | h_1 h_2> \) is a 16 x 16 unitary matrix.

The antisymmetrization is more involved but straightforward if one considers the simply-coupled basis and goes into the centre of mass of the two hydrogen atoms frame of reference. Quoting Berlinsky (Berlinsky), the resulting antisymmetrized wave function is:

\[
\psi_A = \frac{1}{2\sqrt{V}} \phi_I \phi_S (\phi(\mathbf{r}_1 - \mathbf{R}) \phi(\mathbf{r}_2 - \mathbf{R}) + (-1)^S \phi(\mathbf{r}_1 - \mathbf{R}) \phi(\mathbf{r}_2 - \mathbf{R})) \\
\phi(\mathbf{r}_2 - \mathbf{R}_1) \left\{ e^{i \mathbf{q} \cdot (\mathbf{R}_1 - \mathbf{R}_2) / \hbar} + (-1)^S e^{-i \mathbf{q} \cdot (\mathbf{R}_1 - \mathbf{R}_2) / \hbar} \right\} (5-6)
\]

where \( \phi_I, \phi_S \) are spinors, \( \mathbf{\pm q} \) are the momenta of a hydrogen atom in the new frame, and \( \phi(\mathbf{r}-\mathbf{R}) \) is a 1s hydrogen wave function (stands for \( (\pi \mathbf{a}_0)^{-1/2} e^{-|\mathbf{r}-\mathbf{R}|/\mathbf{a}_0} \) in equation (2-2)). In a formal derivation it is convenient to use the projection operator, \( P_S \), which eliminates the undesired states from a general non-symmetrized state, and to sum over all the states. Explicitly, we have:

\[
P_S |\mathbf{P}_1, \mathbf{P}_2; h_1, h_2> = \sum_{\mathbf{q}} \sum_{IM_I} \sum_{SM_S} |\mathbf{q}; SM_S, IM_I> A <\mathbf{q}; SM_S, IM_I | \mathbf{P}_1, \mathbf{P}_2; h_1, h_2> \] (5-7)

where \( |\mathbf{q}; SM_S, IM_I> \) stands for \( |\psi_A> \) as given by (5-6), and \( |\mathbf{P}_1, \mathbf{P}_2; h_1, h_2> \) is the non-symmetrized two-hydrogen atoms state (\( h_1, h_2 \) are the hyperfine states). The matrix element in (5-7) can easily be evaluated and it is approximately given by:
\[ A_{\gamma; S^I M} | p_1, p_2; h_1, h_2 \rangle = \frac{i}{2} A(h_1, h_2; S^I M) \cdot [\delta_{q', q} + (-1)^{S^I I} \delta_{q', -q}] \]  

where \( q' = q_1 = -q_2 \) is the momentum in the special frame mentioned above.

The asymptotic states will then be:

\[ |i\rangle = P_3 | p_1, p_2; h_1, h_2; p_3 \rangle \]  

\[ |f\rangle = |v, \xi, I, M, M^I, k; p_3 \rangle \]  

5-3. The Model

From scattering theory, the total transition rate per unit volume is (see Goldberger and Watson 1964, p. 185):

\[ dR = \alpha d^3k d^3p_3 d^3p_1 d^3p_2 f_H(p_1) f_H(p_2) f_{He}(p_3) \]

\[ \cdot \delta^3(p_3 + k - p_1 - p_2 - p_3) \delta(E_1 + E_2 + E_3 - E_{H_2} - E_{H_3}') \]

\[ \cdot |T_{fi}|^2 \]  

where \( f \)'s are Boltzmann distributions for the momenta of the colliding particles, and \( |T_{fi}|^2 \) is the transition matrix: \( T_{fi} = \langle f | \hat{T} | i \rangle \).

We shall now make the reasonable assumption that the scattering operator, \( \hat{T} \), does not change any of the spin quantum numbers. The spin part can then be factored out and, since the bound state for
$H_2$ requires that $S = M_S = 0$, equation (5-7) and (5-8) yield:

$$|T_{fi}|^2 = |<v,\ell, I, M, \hat{k}; \hat{p}_3 | T |q',0,0; I, M, \hat{p}_3>|^2.$$ 

$$\cdot A^2(h_1, h_2; 00, IM)$$

$$= r(v, \ell, \hat{k}; q_3/q', IM; \hat{p}_3) A^2(h_1, h_2; 00, IM)$$

(5-12)

where $r(v, \ell, k; q_3/q', IM; \hat{p}_3)$ has been introduced to simplify the equations since it will become a parameter of the model. Note that there is no special requirement on the nuclear spin state for recombination to occur, although the rotational quantum number, $\ell$, of the resultant molecule is related to the nuclear spin state by:

$I = \frac{1}{2} (1 - (-1)^\ell)$, where $I = 1$ corresponds to ortho-hydrogen and $I = 0$ to para-hydrogen.

The expression in (5-12) possesses two important features. First, all the field dependence is in the $A^2$ term, which is a matrix. Second, the rate factor, $r$, will explicitly depend on the final state of the molecule. In particular, it depends on $I$, and Berlinsky, Greben and Thomas, who have done preliminary calculations on the rate factor, believe that it is much larger for ortho-hydrogen than for para-hydrogen.

Equations (5-11) and (5-12) can now give us the rate equation which we need. Because we are not interested in any specific momentum, we shall perform the integration over the momenta. We shall assume that $|T_{fi}|^2$, depends only on $I, h_1$ and $h_2 (M_1$ is determined by $h_1$ and $h_2$). If $n_{He}$ is the density of helium atoms, $n_h$ is the density of hydrogen atoms in state $h$, then the recombination
The equation is:

$$\frac{dn_h}{dt} = -n_{He} \sum_I B(I) \sum_{\text{h'}} R^I_{hh'} n_h n_{h'},$$

(5-13)

where $B(I)$ replaces the integration over momenta of the Boltzmann distribution, the delta functions and the rate factor, and where $R^I_{hh'}$ is $A^2$ (see Tables I and II).

A first order solution can be found to (5-13) and it is:

$$n_h = n_h(0)(1 - \frac{t}{\tau_n} + \ldots) = \frac{n_h(0)}{1 + t/\tau_h}$$

(5-14)

where $\tau_h^{-1} \equiv n_{He} \sum_I B(I) \sum_{\text{h'}} R^I_{hh'} n_h(0)$. This establishes the approximate characteristic time of the recombination process.

5-4. Spin-exchange

Rate equations for spin exchange were derived in zero field by Balling et al. (Balling et al. 1964) and generalized by Berlinsky to non-zero field (Berlinsky 1979; Berlinsky and Shizgal 1980). We shall only quote these equations here:

$$n_1 = \frac{1}{2} \{-X(1-X)\gamma_e (n_1^2 e^{-\beta E_{13}} - n_1 n_3^2)$$

$$-2X\gamma_e (n_1^2 e^{-\beta(E_{14} + E_{12})} - n_2 n_4^2)$$

$$-X^2 \gamma_e (n_1^2 e^{-2\beta E_{13}} - n_3^2) - 2X\gamma_o (n_1 n_2 e^{-\beta E_{13}} - n_2 n_3)$$

$$-2[(1-X)\gamma_e + \gamma_o] (n_1 n_3 e^{-\beta(E_{12} + E_{34})} - n_2 n_4)$$

$$-X(1-X)\gamma_e (n_1 n_3 e^{-\beta E_{13}} - n_3^2)$$
\[ -2X\gamma_0 (n_1 n_4 e^{-\beta E_{13} - n_3 n_4}) \]  

\[ \dot{n}_2 = \frac{i}{2} \{ -X\gamma_e (n_2 n_4 - n_1^2 e^{-\beta (E_{12} + E_{14})} \} \]  

\[ -2[(1-X)\gamma_e + \gamma_o](n_2 n_4 - n_1 n_3 e^{-\beta (E_{12} + E_{34})}) \]  

\[ -X\gamma_e (n_2 n_4 e^{-\beta (E_{23} + E_{34})} - n_3^2) \} \]  

\[ \dot{n}_3 = \frac{i}{2} \{ -X(1-X)\gamma_e (n_1 n_3 - n_1^2 e^{-\beta E_{13}}) \} \]  

\[ -2[(1-X)\gamma_e + \gamma_o](n_1 n_3 e^{-\beta (E_{12} + E_{34})} - n_2 n_4) \]  

\[ +X(1-X)\gamma_e (n_3 n_1 e^{-\beta E_{13} - n_3^2}) \]  

\[ -2X\gamma_o (n_3 n_2 - n_1 n_2 e^{-\beta E_{13}}) \]  

\[ -X^2 \gamma_e (n_3 n_1^2 - n_1 n_2^2 e^{-2\beta E_{13}}) \]  

\[ -2X\gamma_e (n_3 n_2 - n_2 n_4 e^{-\beta (E_{23} + E_{34})}) \]  

\[ -2X\gamma_o (n_3 n_4 - n_1 n_4 e^{-\beta E_{13}}) \} \]  

\[ \dot{n}_4 = \dot{n}_2 \]  

where \( E_{ij} \equiv E_j - E_i \) (\( E_j \) is the energy of hyperfine level \( j \)) and

where \( X, \gamma_e \) and \( \gamma_o \) are parameters. \( X = \sin^2 2\theta \) was introduced earlier in Chapter Four, and \( \gamma_e, \gamma_o \) are rate constants for even and odd angular momentum states. The effect of temperature is contained in the factors \( e^{-\beta E} \) introduced by detail balance considerations.
<table>
<thead>
<tr>
<th>$h'$</th>
<th>$h$</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>$\sin^2 \theta \cos^2 \theta$</td>
<td>0</td>
<td>$\frac{1}{4}(\cos^2 \theta - \sin^2 \theta)^2$</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>$\frac{1}{4}$</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>$\frac{1}{4}(\cos^2 \theta - \sin^2 \theta)^2$</td>
<td>0</td>
<td>$\sin^2 \theta \cos^2 \theta$</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>0</td>
<td>$\frac{1}{4}$</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
TABLE - II

RECOMBINATION MATRIX FOR $i = 1 : \mathbf{R}_{hh'}^1$

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>h'</td>
<td>h</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>$\frac{1}{2} \sin^2 \theta$</td>
<td>$\frac{1}{4}$</td>
<td>$\frac{1}{2} \cos^2 \theta$</td>
</tr>
<tr>
<td>2</td>
<td>$\frac{1}{2} \sin^2 \theta$</td>
<td>0</td>
<td>$\frac{1}{2} \cos^2 \theta$</td>
<td>$\frac{1}{4}$</td>
</tr>
<tr>
<td>3</td>
<td>$\frac{1}{4}$</td>
<td>$\frac{1}{2} \cos^2 \theta$</td>
<td>0</td>
<td>$\frac{1}{2} \sin^2 \theta$</td>
</tr>
<tr>
<td>4</td>
<td>$\frac{1}{2} \cos^2 \theta$</td>
<td>$\frac{1}{4}$</td>
<td>$\frac{1}{2} \sin^2 \theta$</td>
<td>0</td>
</tr>
</tbody>
</table>
We can determine $\gamma_e$ and $\gamma_o$ by linearizing equations (5-15) with exponential factors excluded. If we put $\dot{n}_i = (\frac{4}{3} + \delta_i)n_H$, and take the difference $\dot{n}_1 - \dot{n}_3$, then we can obtain an equation similar to equation (2a) of Berlinsky and Shizgal (Berlinsky and Shizgal 1980). The rate constants are:

$\gamma_e = \bar{\sigma} + \bar{v} \frac{n_H}{2}$ and $\gamma_o = \bar{\sigma} - \bar{v} \frac{n_H}{2}$, where $\bar{v}$ is the mean velocity and $\bar{\sigma}$ the thermal average of the cross sections. Using their table I, we can calculate $\gamma_e$ and $\gamma_o$ at different temperatures:

<table>
<thead>
<tr>
<th>T(°K)</th>
<th>$\gamma_e$ (cm$^3$/sec)</th>
<th>$\gamma_o$ (cm$^3$/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.75</td>
<td>$8.081 \times 10^{-13}$</td>
<td>$1.067 \times 10^{-14}$</td>
</tr>
<tr>
<td>1.00</td>
<td>$8.172 \times 10^{-13}$</td>
<td>$1.594 \times 10^{-14}$</td>
</tr>
<tr>
<td>1.25</td>
<td>$8.140 \times 10^{-13}$</td>
<td>$2.025 \times 10^{-14}$</td>
</tr>
<tr>
<td>1.50</td>
<td>$8.056 \times 10^{-13}$</td>
<td>$2.484 \times 10^{-14}$</td>
</tr>
</tbody>
</table>

The range of temperatures of interest to us is from 0.9°K to 1.3°K, so that we can assume that $\gamma_e$ and $\gamma_o$ are effectively independent of the temperature, and we can put:

$\gamma_e = 8.15 \times 10^{-13}$ cm$^3$/sec

$\gamma_o = 1.8 \times 10^{-14}$ cm$^3$/sec

5-5. Results

One important conclusion can be drawn from the approximative solution (5-15): the initial conditions play a crucial role in the recombination process, and unless the relaxation mechanism is efficient (i.e. fast and non-selective), they will determine the evolution of the
hydrogen gas. The characteristic times will depend on the experimental conditions, and the starting point is then to investigate these conditions.

In our experiment, the atoms will be produced in a low temperature discharge (Chapter Seven) and it is then reasonable to assume that the hyperfine states are equally populated. In other words, we assume infinite temperature. Also, the achievable densities in a discharge are above $10^{11}$ atoms/cm$^3$, let us say between $10^{11}$ and $10^{12}$ cm$^{-3}$, and the $^4$He density will be about $10^{18}$-$10^{19}$ cm$^{-3}$. The characteristic time for recombination, as given by (5-2), will be:

$$t_R = (k n_{He} n_H(0))^{-1} = 100-4000 \text{ sec.}$$

On the other hand, spin-exchange has a characteristic time:

$$t_S = (\gamma n_H)^{-1} \approx 1 - 500 \text{ sec.}$$

Thus, spin-exchange tends to be much faster than recombination.

Let us first analyse the zero field case. We note that $\vec{n}_H \equiv (n_1,n_2,n_3,n_4) = (1,1,1,1)$ is an eigenvector of recombination (this is true at all fields), but not of spin-exchange. Thus, the recombination process does not perturb the initial population distribution, although the total density decreases. However, spin-exchange changes the population distribution very rapidly (see figure 5-1) and, subsequently, recombination proceeds with the levels always at equilibrium. The numerical solution is easily understood in terms of a thermal equilibrium situation. Let us call A the case where $B(0) \neq 0$ with $B(1) = 0$ in equation (5-13) and B the case where $B(1) \neq 0$ with $B(0) = 0$.

Case A corresponds to the production of para-hydrogen only, while case B corresponds to the production of ortho-hydrogen only.
In case $A$, equation (5-13) yields:

$$\hat{n}_H/B_{n_{He}} = \frac{1}{4} n_1^2 + \frac{1}{4} n_3^2 + \frac{1}{2} n_2 n_4$$  \hspace{1cm} (5-16)$$

If we assume that thermal equilibrium prevails, then (5-16) becomes:

$$\frac{\hat{n}_H}{B_{n_{He}}} = \frac{\frac{2}{4} \beta a}{\frac{3}{4} \beta a + 3 e} \left( \frac{\frac{1}{4} \beta a}{4} + \frac{\frac{1}{2} \beta a}{4} + \frac{\frac{1}{2} \beta a}{2} \right)$$

$$= \frac{1}{16} \left( 1 + \frac{9}{32} \beta a \right)^2 n_H^2$$  \hspace{1cm} (5-17)$$

A similar procedure for case $B$ gives:

$$\frac{\hat{n}_H}{B_{n_{He}}} = \frac{3}{16} \left( 1 + \frac{29}{64} \beta a \right)^2 n_H^2$$  \hspace{1cm} (5-18)$$

We observe that the effect of the temperature appears only to second order and is almost negligible in both cases ($\beta a^2 = 5 \times 10^{-3}$ at 1 K). Consequently, recombination will proceed as if the relaxation mechanism were ineffective, and $1/n_H$ will change linearly in time (see figure 5-2 and 5-3). The slope of the curve is $B_{n_{He}}/16$ in case $A$, and $3B_{n_{He}}/16$ in case $B$. The experimental value is matched for $B(0) = 16k = 4.48 \times 10^{-32}$ cm$^6$ s$^{-1}$ or $B(1) = 16k/3 = 1.49 \times 10^{-32}$ cm$^6$ s$^{-1}$, and this is confirmed by the numerical solution. Thus, the striking results are that recombination behaves as if there were no relaxation mechanism as long as the (initial) population distribution does not deviate too much from the infinite temperature distribution, and that the hyperfine structure does not make the solution very different from the one given in section 5-1. It is, however, not possible to sort out what is the appropriate contribution of each case ($A$ and $B$) because both of them produce the same result in zero field.

Thus, it is useful to look at the field dependence of the
recombination rate for each case (and, eventually, a mixture of the two cases). We first adjusted the two constants so that the zero field slope corresponded to the experimental value as derived above. Then we looked at the recombination for both cases at $H_0 = 6481$ Gauss and $H_0 = 10$ kGauss, (see figures 5-2 and 5-3). In both cases, the field suppresses the recombination, and we obtained similar curves when $1/n_H$ was plotted against time. The curve starts with the zero field slope and subsequently curves downward, indicating a reduced rate constant. However, the reduction of the recombination rate was larger at 6481 G than it was at 10kG. This unexpected behaviour comes from the dynamics of the hyperfine levels, and the selectivity of the relaxation mechanism. It is not straightforward to sort out the contribution of each case and we would have to investigate their special features, such as the field at which the slowest recombination rate takes place, in order to make the difference between case A and B. We shall not enter into those considerations.

There are a few important conclusions to draw here. First, although the initial conditions are crucial, the dynamics induced by the relaxation mechanism is also important and is intimately related to the recombination problem. Second, it is difficult to separate the effect of each case (production of ortho-hydrogen or production of para-hydrogen) when the hyperfine levels are equally populated initially. Third, the assumed initial conditions give rise to simple behaviour for the recombination. In zero field, the recombination rate is weakly affected by the relaxation mechanism, and, as the field is increased, recombination tends toward a reduced rate.

There is more work to be done on this model, but we need a better
Figure 5-1: Evolution of the population of the hyperfine levels starting with all levels equally populated and in zero field. The broken line the thermal equilibrium distribution.
Figure 5-2: Evolution of the hydrogen atom density for different fields in case A.

\[ n_{\text{He}} = 5 \times 10^{18} \text{ cm}^{-3} \]
\[ n_H(0) = 5 \times 10^{12} \text{ cm}^{-3} \]
\[ B(1) = 0 \]
Figure 5-3: Evolution of the hydrogen atom density for different fields in the case B.
understanding of the experimental conditions.

We shall close this chapter with an illustration of the effect of the initial conditions. Consider the case in which one starts with thermal equilibrium populations of the hyperfine levels, and consider two fields: \( H_o = 405 \) Gauss and \( H_o = 6.5 \) kGauss, while letting \( B(0) = 0 \), (Case B). The effect of the application of a field is much larger (see figure 5-4). This case corresponds to most predictions, since one usually expects that the hyperfine levels will reach their low temperature populations for which recombination is slow at high field. Recombination is suppressed because a \( h=2 \) state atom will not recombine with another \( h=2 \) state atom, and will recombine with a \( h=1 \) atom only because there is an admixture of up electronic spin in the \( h=1 \) state which decreases as the magnetic field is increased.
Figure 5-4: Illustration of the reduction of the recombination rate when thermal equilibrium conditions are assumed.
CHAPTER SIX

THE 765 MHz EXPERIMENT

This experiment was designed for the study of the influence of the magnetic field on the recombination rates and spin exchange, and MR is used as a probing technique (see Chapter Three).

When we look at the hyperfine levels of the hydrogen atom (see Fig. 2-11, we see a very shallow minimum in the separation between the two bottom levels occurring at 6,481 G. The idea is to use that set of levels for MR studies since it is not very sensitive to the homogeneity or the exact value of the static magnetic field. This is an important consideration because we are in fact observing a signal which, as we shall see below, is very weak and because the magnetic field is not shimmed when we first look for a signal. The frequency of this transition is 765 MHz, and requires a transverse magnetic field. Even if 6.5 kG is not an ideally strong magnetic field, it is still possible to bring the field to higher values, at the expense of losing temporarily the signal, and then come back to see what happened in the intervening time.

We also find that there is another transition at 765 MHz which occurs between levels 2 and 3 at a field of 405 G. This transition possesses an effective magnetic moment much higher than for the 1-2 transition ($\mu_{23} = 22.2 \, \mu_{12}$) but is much more sensitive to the experimental conditions, such as the homogeneity of the static field. It nevertheless provides one extra field where the atoms can be "seen".

We shall now go into the listing of a set of data concerning
this experiment, together with some predictions.

6-1. The Two Transitions

It is easily derived that the shallow minimum between levels 1 and 2 occurs at:

\[ H_0 = \frac{a(\mu_e - \mu_p)}{2\sqrt{\mu_e \mu_p} (\mu_e + \mu_p)} = \frac{a}{2\sqrt{\mu_e}} \frac{(1-\eta)}{(1+\eta)^{1/2}} \]  \hspace{1cm} (6-1)

where \( \eta \equiv \mu_p / \mu_e \) (see Chapter Two).

Substituting the numbers in this expression, we get:

\[ H_0 = 6481 \text{ G.} \]

Substituting equation (6-1) into the expression for the energy difference, we obtain that the corresponding frequency is:

\[ f_0 = \frac{a}{2\hbar} \left[ 1 + \frac{2\eta^{1/2}}{1+\eta} \right] \]  \hspace{1cm} (6-2)

\[ = 765483207.7 \text{ Hz.} \]

The low field corresponding to the other 765 MHz transition, which occurs between levels 2 and 3, is given by:

\[ H_0' = \frac{a}{2\mu_e \eta} \left\{ -(1-\eta)(1 + \frac{\eta^{1/2}}{1+\eta}) + (1 + \eta^{1/2})(1 + \eta)^{1/2} \right\} \]  \hspace{1cm} (6-3)

\[ = 404.76 \text{ G.} \]

6-2. Sensitivity to Field Homogeneity

Any inhomogeneity of the static magnetic field will result in a spreading of the resonance frequency of the atoms. It
is therefore worthwhile looking at the sensitivity of the resonance frequency to the field for each transition.

It was mentioned above that the 765 MHz transition at 6.5 kG is rather insensitive to changes in the static field because it corresponds to a shallow minimum. The broadening, $\delta f$, of the resonance frequency is easily obtained by a Taylor's series expansion about $H_0 + \Delta H$, where $\Delta H$ is the difference between the actual field and the resonance $H_0$ (see Whitehead 1979), and we keep only the lowest order terms:

$$\delta f = 1.31 (Hz G^{-2}) (2 \Delta H S_H + (\delta H)^2)$$

(6-4)

where $\delta H$ is the magnitude of the inhomogeneity. If $\Delta H = 0$ and if $\delta H \sim 10^{-6} H$, then $\delta f \approx 5.5 \times 10^{-5}$ Hz, a broadening which is negligible in our experiment.

The situation will be significantly different in the case of the transition at 405 G, for two reasons: the effective magnetic moment is larger, and one is not at a turning point for the frequency. Applying the same procedure as before to this transition we obtain:

$$\delta f = [1.32 \times 10^{-3} (\frac{MHz}{G}) \Delta H + 2.2757 (\frac{MHz}{G}) \delta H$$

(6-5)

If $\Delta H = 0$ and $\delta H \approx 10^{-6}$ H, then $\delta f \approx 1$ kHz. This is more than noticeable, and great care will have to be taken in designing and building the experiment in order to minimize the effect of this limitation.
6-3. **Effective Magnetic Moments**

In Chapter Three, we derived an expression for the effective magnetic moment for the various pairs of hyperfine levels between which transitions can be induced by a transverse oscillating magnetic field, (equation (3-19)). The two effective moments which we need are:

\[ \mu_{12} = \mu \frac{\sin\theta + \mu \cos\theta}{e_p} \]

\[ = 7.5146 \times 10^{-22} \text{ erg/G} \quad (6-6) \]

\[ = 0.11341 \text{ MHz/G} \quad \text{(at 6.5 kg : } \theta = 2.232^\circ) \]

and

\[ \mu_{23} = -\mu \frac{\cos\theta}{e_p} + \mu \sin\theta \]

\[ = -1.6725 \times 10^{-20} \text{ erg/G} \quad (6-7) \]

\[ = -2.5240 \text{ MHz/G} \quad \text{(at 405 G : } \theta = 25.67^\circ) \]

The ratio between these two moments is \( \mu_{23}/\mu_{12} = -22.2 \), which explains why the transition at 405 G is still appealing despite all the other difficulties.

6-4. **Strength of the Signal**

It is very important to estimate the strength of the signal to be detected by the spectrometer, because the sensitivity of the spectrometer is finite and because signal averaging may be difficult for these measurements since \( T_1 \) may be very long.
In Chapter Four we derived an expression (equation (4-20)) which related the power transmitted in the line by the atoms to their oscillating magnetization:

\[ <P_L> = \frac{n^2 m^2 \omega_0 c}{16\beta} \]  

(6-8)

As we know, the total magnetization decays and so does the power emitted. We shall therefore restrict our investigation to the initial signal.

The initial magnetization after a \( \pi/2 \)-pulse is given by equation (3-14):

\[ m(0) = N_H u_{\text{eff}} \text{Tr}[\rho(0)S_x] \]  

(6-9)

where \( N_H \) is the total number of atoms. The question is now: what is the initial average density matrix? In this experiment the atoms are produced by a low temperature discharge which essentially leaves them with an infinite temperature. This leads to no signal at all because we need a population difference in order to have a non-zero value of \( <S_x> \) after a \( \pi/2 \)-pulse. We therefore have to wait until the gas has cooled down, creating the population difference which is necessary for any signal. The mechanisms which perform the cooling are called the spin lattice relaxation mechanisms or simply \( T_1 \)-mechanisms. We saw in Chapter Four that thermal equilibrium is not easily attained in a gas of hydrogen atoms or, in other words, \( T_1 \) is very long. Nevertheless, suppose that thermal equilibrium is fully attained, and that all atoms are uncorrelated, which is generally true. Then:
\[ \bar{\rho}(0) = \begin{pmatrix} P_a & 0 \\ 0 & P_b \end{pmatrix} \]  \hspace{1cm} (6-10)

where \( P_a \) and \( P_b \) are the thermal populations as given by the Boltzmann distribution.

Therefore the total magnetization is:

\[ m(0) = N_H \frac{\mu_{\text{eff}}}{2} (P_a - P_b) \]  \hspace{1cm} (6-11)

The Boltzmann distribution is merely:

\[ P_i = \frac{e^{-E_i/k_B T}}{\sum_i e^{-E_i/k_B T}} \]  \hspace{1cm} (6-12)

By making use of equation (6-12) we can make a table of the population distribution among the four hyperfine levels for different temperatures and magnetic fields. In table III is listed the population distribution at 1°K and 1.5°K, for the two fields of interest to us.

From that, we can extract the values of the maximum magnetization per atom, \( m/N_H \), which will be used together with (6-11) and (6-8) for determining the strength of the signal. This is listed in the following:

\[
\begin{array}{ccc}
T & 1°K & 1.5°K \\
\hline
H_o = 6.5 \text{ kG} & 4.870 & 2.953 \\
\hline
H_o = 405 \text{ G} & -76.10 & -50.93
\end{array}
\]

\[
\frac{m}{N_H}
\]

in \( 10^{-24} \) erg/Gauss.
If we assume the following quantities: \( Q_c = 1000, \eta = 0.2, \omega = 2\pi \times 765 \text{ MHz}, \beta = V_R/8\pi \approx 0.1 \text{ cm}^3 \) and \( N_H = 5 \times 10^{12} \), and substitute them into equation (6-8) we obtain for \( <P_L> \):

\[
\begin{align*}
T &= 1^\circ K \quad 1.5^\circ K \\
\begin{array}{ccc}
H_o &= 6.5 \text{ kG} & 0.0071 & 0.0026 \\
H_o &= 405 \text{ G} & 1.74 & 0.779 \\
\end{array}
\end{align*}
\]

in \( 10^{-14} \text{ watt} \).

The difference between the two transitions available is striking, and it is not necessary to emphasize this point anymore.

The spectrometer which we shall use (Whitehead 1979) has a measured noise temperature, \( T_N \), of about 100°K. In order to see the signal without signal averaging, we need a signal to noise ratio, \( S/N \), of about 5. We then need to have:

\[ (S/N)_P = \frac{P}{P_N} = \frac{P}{kT_N\Delta f} \approx 5 \]  

(6-13)

Suppose that the signal decays in about 1 msec, which is a good estimate when the field is shimmed, then \( \Delta f \approx 160 \text{ Hz} \) and \( P \approx 10^{-18} \text{ watt} \). Thus, the spectrometer can detect the atoms, but we rely on a sufficient shimming of the magnetic field in order to see our first signal. However, the density is also a decisive factor since the power scales like \( n_H^2 \). It is unlikely that \( n_H \) will exceed \( 10^{14} \text{ cm}^{-3} \), but this is more than enough to make it easily observable.
TABLE - III

POPULATION OF THE HYPERFINE LEVELS AT 1°K AND 1.5°K AND FOR $H_0 = 405$ G AND $H_0 = 6.5$ kG.

<table>
<thead>
<tr>
<th>T</th>
<th>h</th>
<th>$P_h(\text{H} = 405 \text{G})$</th>
<th>$P_h(\text{H} = 6.5 \text{kG})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1°K</td>
<td>1</td>
<td>0.26543</td>
<td>0.35919</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.25234</td>
<td>0.34623</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.24324</td>
<td>0.14960</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.23899</td>
<td>0.14497</td>
</tr>
<tr>
<td>1.5°K</td>
<td>1</td>
<td>0.26023</td>
<td>0.32471</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.25161</td>
<td>0.31685</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.24552</td>
<td>0.18110</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.24265</td>
<td>0.17734</td>
</tr>
</tbody>
</table>
6-5. Expected $\frac{\pi}{2}$-Pulse

The width of a $\frac{\pi}{2}$-pulse is given by equation (3-20):

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

where $\omega_1 = \frac{\mu H_1}{2\hbar}$. We know everything but $H_1$. However, in Chapter Four, we derived a relationship between $H_1, <P_L>$ and the parameters of the resonator (equation (4-12)). Substituting that into the expression for $\tau_{\frac{\pi}{2}}$, we obtain the useful formula:

$$\tau_{\frac{\pi}{2}} = \frac{\pi h}{\mu} \left( \frac{\beta \omega}{Q_c <P_L>} \right)^{\frac{1}{2}}$$

(6-14)

During a $\pi/2$-pulse, the energy is supplied by the spectrometer which delivers about 6.3 mW (measured). Assuming this number and the quantities of section 6-4, we can estimate the required length of the $\pi/2$-pulses:

$$\tau_{\frac{\pi}{2}} (405G) \approx 0.45 \mu\text{sec}$$

$$\tau_{\frac{\pi}{2}} (6.5\text{kG}) \approx 10 \mu\text{sec}.$$
CHAPTER SEVEN

EXPERIMENTAL APPARATUS

7-1. Principle

The aim of this experiment is to measure the field and temperature dependence of the bulk recombination rate and the spin-exchange cross-section of the hydrogen atom gas. The principle of the experiment can be summarized as follows.

Upon the application of a static and homogeneous magnetic field, $H_0$, the hyperfine levels of the hydrogen atom split (see Chapter Two), thereby changing both the available transition frequencies and the recombination rates. With the available 765 MHz spectrometer, there are transitions accessible at 405 Gauss and 6.5 kGauss suitable for magnetic resonance studies, which provide information on relaxation mechanisms, recombination rates and absolute densities of atoms. The range of temperatures in which we are first interested is from about 0.9°K to 1.3°K. In this range, the helium atom density is high enough to make $H+H+He\rightarrow H_2+He$ the dominant recombination mechanism without inducing too high a rate. The walls of the closed cell containing the sample will be coated with a film of superfluid $^4He$ in order to prevent wall recombination. The binding energy of the hydrogen atoms on $^4He$ is 0.9±0.05°K (see Morrow et al.) which is low enough to have a small effect on this experiment. The hydrogen atoms will be produced in situ by a low-temperature RF discharge which can produce densities above $10^{12}$ cm$^{-3}$. The protective film is affected by the discharges, but the extent of the damage can be...
controlled by an appropriate choice of the repetition rate and of the power in the discharge pulse. Moreover, if the local rise in temperature is not too high, the film will quickly run towards the warm area and equilibrate the temperature.

Temperatures below 4.2°K are obtained in this experiment by pumping on a bath of liquid \(^4\)He in which are immersed the sample and the resonator. The pot, which contains the liquid helium bath, is placed inside a vacuum can and a (controllable) vacuum is established. This isolates thermally the inner pot from the external bath of liquid helium which is used for maintaining the superconducting magnet in its superconducting state, and which is also used as a supply for the inner pot. This magnet produces the static magnetic field which can be as high as 45 kG.

7-2. Cryostat

The following description refers to figures 7-1 and 7-2.

The cryostat consists of two pots in the region of the magnet, a liquid helium valve and a series of tubes leading to room temperature, where connections are made to the electronics and the pumps. The pots are simply two closed aluminum cylinders. The outer one fits nicely in the bore of the magnet (in fact, the bore of the shim coil device) and the inner one is large enough to contain a rather large resonator. Aluminum has been chosen as a construction material because of its very low magnetic susceptibility which is necessary if we are to achieve a very high field homogeneity. Each pot consists of a flange and a removable part. Both flanges are rigidly held together by most of the tubing. Indium wire is
used as gaskets for sealing the removable part to the flange. Brass screws are used for making these joints since their thermal contraction is similar to aluminum, while at the same time they have strength and are reasonably non-magnetic. The procedure for making a seal will be described later.

All permanent joints are epoxied with Stycast 2850-FT whose thermal contraction is matched to brass but which also works well with aluminum. The surfaces of both the tubing and the aluminum had to be sand-blasted prior to epoxying for reliable bonding.

There are six stainless steel tubes going through both flanges and an additional one going through the outer pot's flange only. The latter is 3/8 in. diameter tubing for making a vacuum between the two pots and terminates with a SV8 valve on the top of the cryostat. The central tube is for pumping on the liquid helium bath in the inner pot. This tubing was originally ¼" diameter all the way up to the top of the cryostat, but has now been enlarged over most of its length in order to increase the pumping speed. It is covered in the bottom with a flux limiting hollow cap which serves to limit the flow of the superfluid helium while allowing fast pumping speed. Two of the remaining tubes, which are 3/16" in diameter, are for the resonator. One contains a stainless steel coaxial cable which carries the signal and which can be moved up and down in order to adjust the coupling. The other one contains a 1/8" diameter stainless steel tube which can also be moved up and down and which is for the tuning of the resonator. On the top flange, both of them are held by an adjustment device which can move the coaxial cable, on the inner tube, up and down very smoothly. Another 3/16" diameter
tube contains an optical fiber which is used for observing the
discharge. It is terminated, at the top, by a sensitive light
detector (a MFPD100 diode) which is connected to a preamplifier.
One of the tubes is in fact a coaxial cable which carries the RF-
pulses for the low temperature discharge. It stops about 1'' below
the flange of the inner can (because the stainless steel coaxial
cable is magnetic) and a copper coaxial cable is connected to it
for the remaining distance to the discharge circuit. Finally,
there is a short 1/4'' diameter tube which is connected to the liquid
helium valve and which allows refilling of the inner pot with liquid
helium. The valve itself sits 3 inches above the outer can's
flange. Care was taken to shorten the tubes extending inside the
inner can as much as possible, because of the field homogeneity
problem. Moreover, thin wall tubing was used wherever possible,
in order to reduce the heat load on the main liquid helium bath
and especially on the inner pot which has a small capacity.

A set of seven wires are fed through both flanges, allowing
electrical connections to the resistors inside. These feed throughs
are #18 copper wire about 1'' long. The varnish was removed at each
end of the wires, which were then epoxied into holes through the
flanges. On the upper flange, these wires are connected to a 9-pin
connector (Amphenol 126 series Hex.), in order to avoid frequent
soldering.

The liquid helium valve is basically just a stainless-steel
needle and a round hole with square edges. A sinter element (#7) is
used as a filter to prevent solid matter from entering into the valve
and damaging it. All the body, including the valve seat, is made
Figure 7-1: Overall view of the cryostat.
Figure 7-2: Detail of the bottom part of the cryostat.
out of brass. It is soldered to the stainless steel tube and is held rigidly by the central tube in order to prevent excessive torque on the epoxy joint at the flange.

All joints to the inner pot are vacuum tight. In particular, the light detector and the adjusting devices include O-ring seals. We previously mentioned one precaution for limiting the flux of superfluid helium. The short tube leading to the liquid helium valve also has a restriction in the bottom for that reason. Moreover, both of the sliding parts, which were described above, have sleeves around them at the bottom where they extend out of the tubes.

7-3. The Resonator

The geometry of the cryostat does not permit the use of the usual coil-capacitor resonator, because the exciting field has to be perpendicular to the static field. We therefore decided to use the "Slotted-Tube Resonator" or STR (see Schneider et al. 1977). It is, basically, just a quarter-wavelength balanced transmission line short circuited at one end. This transmission line consists of an outer, "field limiting", cylindrical conductor and an inner slotted tube (see figure 7-4).

This cavity has two modes which are almost degenerate. The first one, which we do not want, is the "even" mode which corresponds to the normal mode of a coaxial transmission line. The second one, which is the desired one, is the "odd" mode which yields a magnetic field in the centre of the slotted tube. In the even mode, the current flows along both "wings" or "arms" of the slotted tube symmetrically. A current starting at the free end of the
slotted tube flows down and then creeps along the shield (see figure 7-3-a). As we can see, this mode is easily eliminated by removing the cylindrical shield. The odd mode is very different. The current in each arm flows in opposition. If it goes up in one wing, then it goes down in the other. The existence of this mode does not depend on the presence of the cylindrical shield which is there only for limiting the magnetic field to a smaller volume and for maintaining a large Q factor (see figure 7-3-b).

Since the modes are almost degenerate, it is difficult to couple to one mode without coupling to the other. In practice one observes a mixture of the two modes, i.e. there are still two modes, but they are no longer pure. It is important to decouple the two modes as much as possible, not so much because the homogeneity of the resulting magnetic field is affected, but because the filling factor is significantly reduced since the even mode has most of its field between the shield and the slotted tube.

According to Schneider et al., the homogeneity of the rf-magnetic field is optimized when the slot in the inner tube obeys the relationship: \( S = 0.77 \, D \), where \( S \) is the size of the slot and \( D \) the diameter of the slotted tube. They also suggest to use a shield with diameter 2D.

Many trials were made to achieve good decoupling of the two modes, and a convenient design was finally reached, which offers the advantage that the resonator is simple and compact. The first thing to notice is that the inner tube is not slotted all the way down. This will have the effect of shifting the frequency of the even mode with respect to the odd mode. Neglecting end effects, we can
make a crude estimate of this shift by considering the quarter-wave-length for each mode, and this gives a shift of about 140 MHz. The tuning is done by moving a thick metallic (aluminum) cylinder between the inner and the outer tube. Similarly, the coupling is done by moving the coaxial cable which carries the signal. Notice, also, that the whole resonator is made out of aluminum and that a minimum number of screws have been used for fixing removable pieces.

The rf-magnetic field in the slotted tube varies as $\cos^2(2\pi x/\lambda)$, where $x$ is the distance from the short in the bottom of the slotted tube, and $\lambda$ is the wavelength. Therefore, the "centre" of the resonator is near the short. For reasons to be explained in the next section, there is a hole in this short. This has the effect of modifying the magnetic field in that region, while reducing the Q of the resonator since the current is compelled to flow in the corners where the slotted tube meets the short. It nevertheless should not be such a limiting factor compared to the problems caused by the mixing of the modes and the achievement of reasonably high atom densities.

It is easy to obtain a quality factor of about 500 at room temperature, and the final design achieves a Q above 700. This resonator has been designed and built carefully for maximizing its Q. For that reason, all surfaces were smoothed and polished.

The resonator is held by two supports, which allow some adjustment, and great care was taken in the positioning of the center of the resonator with respect to the centre of the magnet. Furthermore, we estimated to what extent the various pieces of the assembly would contract on cooling, because this can significantly change the
Figure 7-3: a) Current path for the even mode,

b) Current path for the odd mode.
Figure 7-4: Resonator design.
setting. The total contraction turns out to be about 5 mm, and the
centre of the magnet has to be located at least that amount above
the desired centre of the resonator which we chose to be 0.6" above
the bottom of the slotted tube.

7-4. Low Temperature Discharge

A low temperature discharge is used for producing the atoms in
this experiment. The discharge resonator, which operates at 70 MHz,
is just a coil and a capacitor in parallel, and the cell fits in
the bore of the coil. This cell contains a mixture of helium and
molecular hydrogen. It is filled at room temperature with about
half an atmosphere of helium and half an atmosphere of hydrogen gas.

It was not a trivial matter to design the discharge resonator
because it has to work in a rather intense magnetic field and because
it has to start by itself without external triggering source such as
a Tesla coil. It was found in the zero field experiment that trans­
former coupling to this resonator seemed to work well. This is
easily realized by winding about one turn of primary coil around
the resonator coil which contains about ten turns. We nevertheless
have to watch for possible arcing which can damage the capacitor
or the coil. It was also verified, at room temperature, that for
best performance the axis of the coil should be parallel to the
axis of the magnet, a characteristic which suits us.

The discharge circuit is located beneath the 765 MHz resonator,
in a closed metallic container. We can see on figure 7-4 that a
channel, about 0.9" long, separates the slotted tube from the
discharge. This channel has two purposes. First, the cell can
slide in, and atoms created by the discharge will diffuse to the probing region. Second, it is well beyond cut-off for the RF of the discharge and helps to reduce its propagation into the resonator. The source of RF is an Arenberg pulsed RF generator which possesses the useful feature that the frequency can be varied over a wide range, which allows us to use a fixed frequency discharge circuit.

It is worth mentioning that all electrical soldered joints were made out of indium, although they were tin-lead previously. This is because the critical field for indium is below 405 Gauss where our low field, homogeneity sensitive, transition takes place. It is in fact highly undesirable to have a superconductor close to the probing region because of its diamagnetism.

7-5. **Temperature Measurement and Control**

In this experiment, calibrated resistors are used for measuring the temperature and for sensing the liquid helium. One of them (120 Ω nominal) is located on one of the rods, which support the magnet, about 2 cm above the top of the magnet. It serves two purposes. One, it gives the ambient temperature in the bore of the dewar. Two, it is useful for determining the level of the liquid helium which should never be too close to the magnet. Another one (100 Ω nominal) is located on the liquid helium valve. It serves the same purposes as the other except that it is cm higher. A third one (210 Ω nominal) is precisely calibrated in zero field and is located inside the inner pot, above the resonator. This one gives the temperature of the inner pot and allows us to calculate the helium gas density in the cell, \( n_{\text{He}} \), since \( n_{\text{He}} \) is
precisely related to the temperature. Another precisely calibrated resistor will be added in the inner pot for comparison purposes in the next run.

The temperature is controlled in two ways. First, the cooling is done in the pot by pumping on liquid helium. This should bring it down to almost 1°K. Second, a heater (90 Ω at 1°K) can be used for raising the temperature or for studying the behaviour of the inner pot under finite heat load. This heater is .003" brass wire folded, twisted and then wound around the outer surface of the inner can. The wire is folded in order to avoid the induction of a magnetic field when the heater is on. Armstrong A-12 epoxy is used for gluing.

7-6. Indium Seal

The indium seals, described above, are made as follows. The surfaces of both the flange and the removable can are cleaned first with tetrachloroethylene which removes the grease and part of the oxide. Then, a small amount of Apiezon-M grease is applied to both surfaces, especially in the corner where the indium wire sits, to prevent sticking to the aluminum. Two indium wires are then wound around the joint, one on top of the other, and the ends are crossed. One can now slide the removable can in the flange and screw it tightly.

7-7. Experimental Procedure

The dewar, which we use in this experiment, is a large volume stainless steel dewar whose bore is 9 inches in diameter and
whose depth is 4 feet. It therefore has a large thermal inertia and a special procedure has been devised for cooling it.

It is supported by a wooden rack which possesses a pulley assembly allowing raising and lowering of the dewar. The magnet is supported by three rods which are screwed on an aluminum flange, which sits on the top of the dewar. Finally, the cryostat slides in the middle of that flange which has a large hole in its centre. The cryostat can be taken out independently from everything else, even when the dewar is mounted and cold. This is an advantageous feature which allows modifications on the cryostat while the cryostat is still cold or while it contains liquid nitrogen.

The cooling procedure goes in a few steps. First, one flushes the bore with gaseous nitrogen a few times and then transfers liquid nitrogen in the liquid nitrogen jacket. After several hours, the inside is very cold and one adds liquid nitrogen to the central region of the dewar. This first step is there only to avoid thermal shock and stress on the cryostat. One waits again for about twelve hours and then starts to transfer the liquid nitrogen out of the dewar by applying pressure inside. Then, one pumps on the remaining liquid nitrogen and obtains further cooling of the magnet. Finally, one can transfer liquid helium into the dewar.

The liquid helium valve is now open so that cold helium gas can flow in and cool the inner pot down. When the liquid helium level is high enough, it starts to fill the inner pot if one applies a slight under pressure inside. Resistors are used (see section 7-6) for detecting the liquid helium level. There is one
on the valve and one inside, above the resonator.

The next step is to pump on the liquid helium bath in the pot for cooling it down to 1°K.

7-8. Performance

Because of their fragility, it took several trials before we succeeded in achieving permanent epoxy joints, but the cryostat can now be cycled without any mechanical problem. However, we could not lower the temperature below 1.15°K by pumping on the liquid helium bath, and there are a few reasons for this.

We have estimated a maximum heat load of 30 mW. This is fairly small, but contributes to the limitation of the cooling. The creeping superfluid helium is the source of another heat leak, and this is why we have added pieces which limit the flow of superfluid to the outside. We also estimated the pumping speed and we can conclude that, first, the restriction in the bottom of the pumping line, which previously was made out of teflon, added too much impedance on the pumping line, and, second, the line itself was too small. Although the main problem was the restriction, we decided to modify both of them. We have not yet tried the cryostat with these improvements.

Although we cannot be definite at this point, it seemed that the liquid Helium valve was behaving normally but that there was intermittent leakage through the seal. However, if there was a leak, it was very small most of the time and did not perturb the experiment.

The low temperature discharge worked without any difficulty,
even at low power. We observed a narrow resonance frequency (about 1 MHz) which indicates a high Q. The light detector was easily detecting the signal from the discharge even if the geometry was not optimized in that respect. We could observe the effect of the discharge intensity, either more power or faster repetition rate, on the temperature in the inner pot which started to rise slowly following an increase in intensity.

As expected, the Q of the 765 MHz resonator increased as the temperature was lowered, and we measured a Q of about 800 at 4.2°K. We hope that the new resonator will offer a Q above 1000 at this same temperature. The tuning and the coupling offered no difficulty.

We did not see a signal, but this was not a complete surprise because one requires the best experimental conditions which we did not have. We nevertheless hope that we will be able to detect the hydrogen atoms in the next run, once all the necessary modifications have been made.
In this experiment, it is essential to achieve a signal to noise ratio larger than one for a single free induction decay, because signal averaging may not be possible (Chapter Six and Four). Many factors contribute to limit the S/N ratio, such as the noise figure of the spectrometer, the Q and the filling factors of the resonator, the density of hydrogen atoms and the homogeneity of the magnet. In this appendix, we shall be concerned with the magnet homogeneity.

The S/N ratio is inversely proportional to the homogeneity of the magnet. Indeed, an inhomogeneous magnetic field will induce a superimposed $T_2$ mechanism which will accelerate the decay of the signal (Chapter Four) and this compels us to use a wider frequency band for observing the signal, thereby reducing the signal to noise ratio. Furthermore, this faster decay of the signal quenches the relaxation mechanisms which we want to study. For these reasons, it is a basic requirement to achieve a highly homogeneous static magnetic field.

The superconducting magnet used in this experiment has a rated resolution of 1 parts in $10^7$ for a 5 mm sample tube. This quantity has been calculated using the halfwidth of the lineshape of a magnetic resonance signal. However, the manufacturer obtained a strongly peaked lineshape with substantial wings and used it for calculating the resolution. Such a lineshape is equivalent to having a high homogeneity in a small region around the centre of the magnet and a poor homogeneity outside. Our aim is, however,
to obtain high homogeneity over a larger volume, and this cannot be achieved by adjusting the first order shim coils built into the magnet.

We can improve on the homogeneity in two ways: either by averaging the field by spinning the sample around the main axis, or by shimming the field using higher-order correction coils appropriately designed. The former approach is not practical for our gaseous samples, and we shall adopt the latter approach.

**PRINCIPLE OF THE SHIM COILS**

Any field can be expressed mathematically in terms of a complete set of functions, each one of which has a specific symmetry. Initially, the field in a high resolution magnet is fairly homogeneous and imperfections to it are usually very small. In practice, when one expands the observed derivation in a series, one finds that the importance of a term goes inversely with its order.

The idea of shimming the field relies on the fact that we can eliminate the first few terms by adding fields of the same symmetry but opposite sign, leaving only the homogeneous term plus terms of higher order which should be weaker. It is not practical to add correcting fields for each spatial component of the field. For example, this would require nine coils just for the first order set. What is usually done is to correct for the axial or z-component of the field, in which we are interested, if the main is along that axis. We can justify this choice in two ways. On the one hand, one can argue that correcting for one component suffices to bring
the other two in the right direction. On the other hand, one can compare the importance of the radial components of the imperfections to the axial one, and find that the latter contributes more to the homogeneity than the former. To see this argument, let us write the actual field in the bore of the magnet as \( \vec{B} = \hat{B}_0 + \vec{B}' \), where \( \hat{B}_0 \) is the perfectly homogeneous field along \( \hat{z} \), and \( \vec{B}' \) is a small imperfection to it. Thus, remembering that \( B' \ll B \),

\[
|\vec{B}| = |\vec{B}_0 + \vec{B}'| = [(B_0^2 + B_y^2 + B_x^2) + B_y B_x]^{1/2}
\]

\[= B_0 + B_y \frac{B_x^2 + B_y^2}{2B_0^2}\]

Thus, components \( B_y \) and \( B_x \) do not contribute significantly to the field inhomogeneity compared to \( B' \), and it suffices to shim only the axial component.

Furthermore, if one cannot achieve a field of a pure symmetry, or order, one can at least design a coil which contains that desired term as the dominant one, plus higher order terms among which one tries to eliminate the first few. In other words, the shimming device consists of a properly designed coil which possesses the desired "term" plus some high order terms which we do not want, of course, but which cannot be eliminated.

**Zeroth, First and Second Order Coils**

The general solution for the potential around the origin is:

\[
V = \sum_{n=1}^{\infty} \sum_{m=0}^{\infty} r^n p^m (\cos \theta)(A_n \cos m\phi + B_n \sin m\phi),
\]
where $A_n^m$ and $B_n^m$ are constants and $p_n^m$ in the nth order associated Legendre polynomial.

This gives for $B_z$:

$$B_z = -\frac{\partial V}{\partial z} = \sum_{n=1}^{\infty} \sum_{m=0}^{n=m} r^{n-1} [(n-m)\cos\theta p_n^m(\cos\theta) + \sin\theta p_{n+1}^m(\cos\theta)].$$

$$\cdot [A_n^m \cos (m\phi) + B_n^m \sin(m\phi)],$$

which, in Cartesian coordinates, becomes:

$$B_z = A_1^0 + 2A_2^0 z + 3A_2^1 x + 3B_2^1 y + \frac{3}{2} A_3^0 (2z^2-x^2-y^2) + 12A_3^1 zx + 12B_3^1 zy +$$

$$+ 15A_3^2 (x^2-y^2) + 30B_3^2 xy + 4A_4^0 [z^2 - \frac{2}{3}(x^2+y^2)] + \frac{15}{2} A_4^1 x(4z^2-x^2-y^2)$$

$$+ \frac{15}{2} B_4^1 y[4z^2-x^2-y^2] + \ldots$$

(see Anderson 1961).

This is our basic equation. We note the important property that we have a series of independent terms. The first term is simply the homogeneous field itself, a constant, which we want to keep. The following three terms, $x$, $y$ and $z$, are the first order imperfection terms which can be corrected for by the coils bearing the same name, namely the $x$, $y$ and $z$ shim coils. These are already available in the magnet, and will not be discussed any further.

The second order terms which are five in number are:

$$2z^2-x^2-y^2$$

(designated by $z^2$ below), $xz$, $yz$, $xy$ and $x^2-y^2$.

We shall now look at all these five terms and how we correct for them.
This is the simplest one and it is discussed first because it exemplifies the method quite well. Together with the $z$-coil, it is termed an axial correction term because of its special symmetry.

A $z^2$ (or, rather, $2z^2-x^2-y^2$) term appears in the series expansion of the field created by a circular loop whose symmetry axis is along the $z$-axis. Practical considerations dictate its use, because it is simple and circular. In fact, it is very easy to wind a wire around a cylinder and it is mechanically strong. Furthermore, we want to take as little room as possible for the coils, and that they are lying close to the bore's surface is great advantage.

The ordering of loops which allows one to eliminate up to the fourth order term, keeping only the $z^2$ dependence, is shown in Fig. A-1-b. It consists of four loops, arranged symmetrically about the $xy$-plane. Equal currents are flowing in the two outer loops and similarly for the two inner loops, even though it is not the same in both sets of loops. This way, we gain reflection symmetry.

The $z$ component of a field due to a circular ring, whose principal axis is along the $z$-axis and whose centre is located at $z_0$, is given by:

$$B_z(r,\theta) = \frac{-\mu_0 i \sin^2 \alpha}{2a} \sum_{n=1}^{\infty} \left( \frac{r}{a} \right)^n \frac{P'_n(\cos \alpha) P_{n-1}(\cos \theta)}{P_n(\cos \alpha)}.$$  \hspace{1cm} (A-1)

(Sauzade and Kan 1973, p. 45).

In this expression (the equation is in SI units), $i$ is the current circulating around the loop. The other parameters are illustrated.
Figure A-1: a) Definitions of the parameters for the description of a field created by a loop.

b) \(Z^2\)-shim coil configuration. In parentheses are given the actual span of the wiring, corresponding to the width.
in Fig. A-1-a.

The reflection symmetry enables us to eliminate the terms which change sign when $z_0$ goes to $-z_0$. In other words, only the even terms remain, namely terms containing $P_0$, $P_2$, ... Of those, we want to keep $P_2(\cos\theta)$, which is just:

$$\frac{1}{2} (3\cos^2\theta - 1) = \frac{1}{2r^2} (2z^2 - x^2 - y^2).$$

The term comprising $P_4(\cos\theta)$ (i.e., $n=5$) vanishes identically when $\cos \alpha$ is one of the roots of $P_5'(x)$. These roots are:

$$x = \pm 0.77, \pm 0.29,$$

leading to

$$\alpha = 40.1^\circ, 73.4^\circ.$$  

Conveniently, there are two sets of loops, each taking one of these angles. In terms of the $z$-position of the centre of the loop these correspond respectively to: 1.19a and 0.30a.

The constant term, containing $P_0(\cos\theta)$, goes away after an appropriate choice of the current intensities. If $I_i$ and $I_o$ are the current flowing in the inner and the outer loop respectively, and similarly for their angles $\alpha_i$ and $\alpha_o$, then we need to fulfill the following condition:

$$-\frac{\mu_o I_i \sin^2 \alpha_i}{2a} p_1'(\cos \alpha_i) = \frac{\mu_o I_o \sin^2 \alpha_o}{2a} p_1'(\cos \alpha_o),$$

or, arranging the terms:
\[
\frac{I_i}{I_o} = \frac{\sin^2 \alpha_i \cos' \alpha_i}{\sin^2 \alpha_i \cos' \alpha_i} = -\frac{\sin^3 \alpha_i}{\sin^3 \alpha_i} = -0.30.
\]

The relative current is adjusted by picking the appropriate ratio for the number of turns.

Actually we have to run wires from one loop to the other in order to feed them using only one circuit. This is done easily if one used the same path for currents of opposite directions and equal intensity. The topology allows it and this is true also for the next four coils. The only problem might be to reduce as much as possible the number of such wire pairs.

**ZX AND ZY COILS**

These two coils go together and they are related by a 90° rotation around the z-axis. Thus it suffices to analyse one of them, say xy.

Here, we use circular arcs as depicted in Fig. A-2-a, which also fit on a cylindrical base. The field created by a circular arc is very complicated, and its form, including terms up to the fourth order, is given in Sauzade and Kan, p. 48-49 (Sauzade and Kan 1973), but there are some mistakes in the expression given.

Stacking eight of these arcs and applying currents as shown in Fig. A-2-b, we gain symmetries and most of the terms drop out. We shall summarize how it proceeds.

The terms not changing sign when \( z_0 \to -z_0 \) are eliminated because of the reflection anti-symmetry. Therefore, up to the fourth order, the terms left are: \( z, xz, z^2, x^2z, y^2z, xz^3, x^3z \)
Figure A-2: a) Parameters of the arc which produces a field around $z_o$.
b) ZY and ZX shim coils configuration. Here is given the configuration for ZX, but a rotation by 90° gives the ZY configuration. In parentheses are given the width of the wiring.
and \(xy^2z\).

Since we have reflection symmetry in the \(zy\) plane, only those terms remain which do not change sign as \(i \rightarrow i\), and \(x \rightarrow -x\). This reduces the set to: \(xz, xz^3, x^3z\) and \(xy^2z\).

Finally, taking \(\theta = 60^\circ\), all three remaining fourth order terms are proportional to the polynomial:

\[4z_0^4 - 41z_0^2a^2 + 18a^4,\]

which vanishes for \(z_0 = \pm 0.68a\) or \(\pm 3.13a\).

The currents in all branches are then equal. The currents running vertically cancel each other by pairs along the \(z\)-axis, leaving only a very weak field at the origin.

**XY AND \(X^2-Y^2\) SHIM COILS**

Once again, they are related to each other by a rotation, the rotation angle being \(45^\circ\). We shall then analyse only one of them: \(x^2-y^2\).

We also make use of circular arcs, but the arrangement is more complicated. The stacking and the directions of the currents are shown in Fig. A-3.

Summarizing, the reflection symmetry about the \(xy\) plane leaves only: \(1, x, x^2, y^2, x^3, xz^2, xy^2, z^4, x^4, y^4, x^2z^2, x^2y^2,\) and \(y^2z^2\).

Since we have opposite arcs about the \(zy\) plane, only terms not changing sign when \(x \rightarrow -x\) stay; so \(x, x^3, xz^2\) and \(xy^2\) disappear.

Applying a similar procedure for the arcs opposite about the \(z-x\) plane (exchanging \(i\) for \(-i\), \(x\) for \(y\) and \(y\) for \(-x\)) we get as remaining terms: \(1, y^2, x^2, z^4, y^4, x^4, y^2z^2, y^2x^2, x^2z^2\).
Figure A-3: XY and $X^2-Y^2$ shim coil configuration. Here is given the configuration for XY, and the $X^2-Y^2$ configuration is obtained by a 90° rotation around the z-axis. In parentheses are given the actual width of the wiring.

$z_2 = 1.93 \ a = 3.049" \ (3.009" - 3.089")$

$z_1 = 0.335 \ a = 0.529" \ (0.489" - 0.569")$
We see that, because we changed $i$ for $-i$ in going from the set along $x$ to the set of arcs along $y$ axis, all common terms will cancel identically, namely $1$, $z^4$ and $y^2x^2$, leaving the difference between the other ones. The undesirable terms, $x^4-y^4$ are $x^2z^2-y^2z^2$, are both proportional to the polynomial:

$$12z^2 - 46z^2a^2 + 40a^4$$

which vanishes for $z_o = \pm 1.93a$ or $\pm 0.335a$.

Finally, the factor $\sin 2\theta$ multiplying the remaining $x^2-y^2$ term is maximized when $\theta = 45^\circ$. This is the angle chosen here. The vertical wires also have very little effect here.

**SHIM COILS AS A PRACTICAL DEVICE**

**Investigate the Problem**

In designing this device, we had to consider a set of constraints because we want to keep as many as possible of the advantageous features of this magnet.

The magnet has, for instance, a rather large bore radius (3.75"), and we wanted to maintain this characteristic. The shim coils described above have a suitable geometry to meet this requirement. Thence we used a piece of aluminum pipe which tightly fit in the bore and which has an inner diameter of 3 inches. Channels were grooved on the outside for accommodating the wires.

The choice of the material is also important here because of the magnetic impurities one might find in it. From Curie's Law we know that these impurities show up very strongly at low temperatures. It seems that the best choices are either aluminum or
copper, albeit aluminum is supposedly better. In practice, both of these materials are found as alloys and one must look at the composition. In spite of this, and for some unexplained reasons, aluminum seems to quench the effect of the magnetic impurities in it. Moreover, since the frame of the magnet is also made of aluminum and since there is a tight fit between the latter and the device, it is preferable to use the same composite material for avoiding contraction problems.

Five shim coils have to sit in very little space, since the supporting cylinder has a wall thickness of only 1/8". Furthermore, the shape of the coils compells us to superimpose them one on top of the other, overlaps being unavoidable, and this is not an easy task.

Finally, we can either run the coils continuously, feeding current through them from the outside all the time, or use superconducting wires and leave them into persistent mode when the required current is flowing in. We chose the second solution, expecting a reduced boil off of liquid helium, although this technique is more complicated. For instance, we had to make use of superconducting switches which we shall describe below.

Design

A sketch of the device is given in Fig. A-4.

It is sitting on top of the magnet which, in passing, is used upside down. This way, switches and wires are further away from the centre of the magnet, reducing perturbations to the field at that site. The aluminum tubing covers the whole length of the
Figure A-4: Shim coil device. A schematic drawing of the aluminum insert containing the shim coils and the superconducting switches. C.M. is the centre of the magnet.
magnet, mainly because some coils are very extended. This pipe has been thinned down all along to fit nicely in the bore and an extra layer (~0.01") has been taken off in the region where the coils sit, allowing further coverage of the work.

The superconducting wire used for the coils is the same as the one in the magnet. It thus has the same features and, for instance, high enough a critical field. The diameter, including coating, is 0.010", and, in principle, five layers could fit one on top of the other without any problem. The wires sit in an array of grooves which have a special depth for each coil. The grooves are coated with a double side tape to help in the winding. Since the coils have to overlap we arranged the order to achieve best mechanical stability. A piece of aluminum foil was wrapped around the coils, providing further strength and protection.

We should mention here that we have to wind many wired turns in order to get the appropriate current ratio and intensities, thereby adding width to all lines of the skim coils. This reduces the accuracy of the correction, although by a very small amount.

The electrical connections and the switches are located in a small box around one end of the cylinder. The superconducting wires are spot-welded together after removal of the copper layer with nitric acid. For convenience, all connections to wires going up to the top of the dewar are done via a 9-pin connector, on the side of the box. The current feeding of the coils is controlled by superconducting switches which we shall describe in the next section.
Most pieces are made of aluminum, even the screws, and the permanent joints are done with epoxy (Armstrong A-12).

Switches

The use of superconducting wires provides us with the possibility of going into persistent mode. This procedure requires superconducting switches.

Their principle is simple. Above a critical temperature, $T_c$, a superconducting material becomes normal, that is it becomes a simple conductor with a finite conductivity. Materials can be found with $T_c$ a few degrees above 4.2°K, thereby requiring a small amount of heat to change their state (or mode). As shown in Fig. A-5-a, a small length of superconducting wire is short-circuiting a coil (one of the shim coils) and a heater is next to it. The whole assembly is immersed in liquid Helium, keeping the small wire in its superconducting state. A current can flow freely around the coil and this small wire and this corresponds to the persistent mode. Conversely, when a little bit of heat is released, following the application of a voltage, the small wire becomes normal and the currents can relax since the coil is now in series with resistive elements. It can thus be adjusted from the outside. Turning the heater off just leaves the selected current in the coil.

In practice, we have to make sure that the heating is efficient, without boiling off too much helium. What we need, in fact, is to reach a peak temperature above $T_c$ in a rather small region. On the other hand, the cooling must be fast enough in going back to the
Figure A-5: 
a) Schematic drawing of a superconducting switch.

b) Physical aspect of a switch.
persistent mode. What we did is to wind a (twisted) superconducting wire, roughly 20 cm long, around a metal glaze resistor (about 200 ohms) which keeps a constant resistivity when the temperature is lowered. Note that the copper layer on the superconducting switch wire was previously removed so that the normal state resistance of the wire is large. The resistor was then enclosed in a teflon capsule, and the remaining space was filled with paraffin wax (see Fig. 4-5-b). The power required to turn the switch on is only 0.3W and the switching time is of the order of a second.

Circuitry

All five coils are wound in series and the choice of the coil, which one wants to change the current flowing in, is done by the switch selected to be turned on (Fig. A-6). That way, only two wires are necessary to carry down the coils' currents. This is important since these wires must carry about 1 amp and therefore have to be made of copper. This procedure has the inconvenience that one cannot rapidly go from one coil to the other, or even adjust two coils at the same time. This would have been an advantage because second order coils make very fine adjustments which are hard to observe.

Since the current for the heater in the switch is small (40 mA), we used #32 brass wire in order to reduce the heat load on the helium bath.
Figure A-6: Circuitry of the coils and the switches.
PERFORMANCES

Using $D_2O$ and $D_2$ probes, designed and made by W.N. Hardy and B.W. Statt, we were able to study the influence of the shim coils on the field homogeneity.

As already mentioned, they have very little effect, and optimization of the field homogeneity is rather tricky. This is actually a good application of the trial and error method, and it takes hours to reach the optimum.

In principle, each coil is independent from the other. However, on a practical basis, they induce currents in each other every time we change the value of one of the currents. The mutual inductance between the second order coils is negligible but the first order coils do induce a current in them. Nevertheless, the procedure is iterative if one starts with the first order ones, the currents induced being very small from the second to the first order.

Another interesting, though not desirable, phenomenon occurred when the current was increased up to about one ampere in the second order shimming circuit. We observed that the circuitry in the protective box could induce a noticeable field at the centre of the magnet, which usually went back to zero when the current was decreased. Sometimes, unfortunately, it did not go back to zero, certainly because the magnetic forces had moved the wires around.

We shall mention that these shimming coils are very sensitive to the "choice" of the centre of the magnet (or, equivalently,
the sample). This is particularly true of the \( z^2 \)-shim which of all the shim coils has the greatest influence onto the field.

We could not thoroughly check the effect of each coil on the magnetic field. However, every coil acts its own way, but only \( z^2 \) showed up clearly the effect which it has on the free induction decay (FID). The \( z^2 \)-shim gives bulk to the first part of the FID while depleting the end of it (see Fig. A-7a). This is a good feature because the observed tendency of the FID was a fast decay in the first few milliseconds followed by a very long slow decaying tail (see Fig. A-7b). Although the other shim coils brought slight improvement in the FID, their specific role could not be sorted out.

The best \( T_2 \) which we obtained was typically 80-100 msec, which can be considered unsatisfactory and there seemed to be spurious \( T_2 \) mechanisms which short-circuited the intrinsic one.
Figure A-7: a) Envelope of a free induction decay which shows the effect of the $z^2$ shim.

b) Initial free induction decay without second order shimming.
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