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Spin Relaxation Studies in He$^3$ Gas by Optical Pumping

by

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My wife, Dotty, to whom this thesis is affectionately dedicated, has my deepest thanks for her patience and understanding.
PART I: RELAXATION PROCESSES IN THE PRESENCE OF AN ELECTRICAL DISCHARGE

I. Introduction

The interaction of an atom with its surroundings has been the subject of frequent and intriguing studies throughout the history of atomic physics. The application of optical pumping techniques to the atoms of helium has provided a method for observing the interaction of the $2^3S_1$ metastable and the $1^1S_0$ ground state atoms of the mass three isotope of helium with their surroundings in a unique environment.

The main text of this thesis is divided into two parts: (a) lifetime limiting processes involving the metastable and ground state He$^3$ atoms in the presence of a weak electrical discharge, and (b) the spin state lifetime of the He$^3$ ground state atom in a closed vessel at low gas pressures. The latter section discusses a new mechanism for spin lattice relaxation which is operative in paramagnetic gases at low densities.

In each of these two major sections the optical pumping process forms an integral part of the experimental procedure and, indeed, the effects to be described would be unobservable without it. In the former case the optical pumping conditions directly determine the metastable and ground state relaxation properties while in the latter case the optical pumping technique coupled with an electron exchange mechanism provides the large nuclear polarization required at low densities to make observable the behavior of the nuclear spins. Consequently, the optical pumping process in He$^3$ is presented in some detail.
The appendices include a detailed calculation of the scattering coefficients for spin exchange in He$^3$ and a discussion devoted to the necessary ingredients of random processes and correlation theory required to justify rigorously some of the steps taken in Part II.
II. Optical Pumping

A. Optical Pumping Defined

For an ensemble of atoms in thermal equilibrium the relative populations $n_j$ of a set of energy levels $E_j$ are specified by the Boltzmann distribution law such that $n_j \propto e^{-E_j/kT}$ where $T$ is the equilibrium temperature of the ensemble. An external agency which forces a change in these populations toward some nonequilibrium value can be thought of as a "pumping" of atoms from one level to another. A variety of methods have been used to produce these changes.

The term "optical pumping" has been applied to the technique proposed by Kastler\(^1\) in 1950 and is often taken to mean the production of an orientation or alignment of spins in a vapor or gas of paramagnetic atoms through the selective removal of atoms from given quantum states by the action of a specially prepared beam of resonance radiation. It was first successfully applied to the case of orientation of sodium atoms in an atomic beam.\(^2\)

In its present form circularly polarized resonance radiation is absorbed as it passes through a paramagnetic gas or vapor whose energy levels are split by an external magnetic field, initiating an excitation-emission cycle. On the average angular momentum is transferred from the resonance light to the atom and if the excitation-deexcitation process is repeated often enough the atoms can be accumulated in the states whose $z$ component of angular momentum, $M_z$, is greatest (or least) provided the atom being pumped has a sufficiently long lifetime. To produce an alignment or orientation different from the Boltzmann distribution it is necessary that the pumping cycle be completed in a time on the order of or shorter than the characteristic time for atoms to thermalize.
Following a suggestion by Dehmelt\textsuperscript{3} the progress of the pumping process can be observed by monitoring the light transmitted through the oriented vapor. Any decrease in the number of atoms in the polarized state provides more absorbing atoms, thus increasing the absorptance of the gas and decreasing the intensity of the transmitted light.

\textbf{B. Historical Summary}

The systems in which the technique of optical pumping have been successfully applied include the ground states of the alkali atoms and the $2^3S_1$ metastable states of the helium isotopes of mass three and four. In these cases the paramagnetism of the pumped states is due to the electronic spin of the atom. The isotopes of mercury have also been optically pumped. Here the paramagnetism is associated with the nuclear spin, the ground state being $^1S_0$.

The degree of polarization obtainable is limited, in general, only by the intensity of available light sources and by the amount of disorientation caused by the collision of polarized atoms with impurities or with walls of the containing vessel. The use of magnetically "inert" wall coatings or the use of nonmagnetic "buffer" gases which inhibit wall diffusion dramatically reduce disorienting collisions. Both techniques are widely used and permit polarizations approaching 100\% to be obtained. Optical pumping in the systems described above and under a variety of conditions are treated in detail by a number of authors.\textsuperscript{4-9}

The angular momentum accumulated by the optically pumped sample may be transferred to other species by a collisional spin-exchange process. Dehmelt\textsuperscript{10} first applied this method to a system of nearly free electrons in collisional contact with optically oriented sodium atoms. The exchange process permits the orientation of hydrogen, nitrogen, tritium,
deuterium atoms among others. The interaction of the optically oriented atoms with their surroundings (walls, buffer gas, etc.) have yielded useful information concerning the cross sections for various types of collisions. And, of course, the paramagnetic properties of these atoms have been examined in detail and extremely precise measurements of hyperfine interactions and g-values made.

C. Optical Pumping in He $^4$

In this section we will describe the optical pumping process in He $^4$. This will provide an introduction to the more complicated case of He $^3$ and at the same time provide additional insight into some measurements which are more easily obtained from optical pumping experiments in He $^4$.

Alignment of the He $^4$ metastable ($2^3S_1$) atom in a weak magnetic field was first reported by Franken and Colegrove $^{11}$ using unpolarized resonance radiation. Further studies utilizing circularly polarized resonance radiation to orient the metastable atom were carried out by the author. $^{12}$

The pumping and monitoring process for optical pumping can be described in terms of the frequency spectrum, direction, and polarization character of the resonance light beam and a set of coefficients which describe the relative probabilities for absorption and reradiation between the metastable state and the $2^3P$ excited states. An energy level diagram of the states participating in the optical pumping process in He $^4$ is shown in Fig. 1. The splittings are appropriate to those of a weak magnetic field.

Experimental observables (see Appendix A) can be related to the population densities of the three magnetic sublevels of the $2^3S_1$
Fig. 1: Energy level diagram of the pertinent energy levels in He$^4$
(not to scale).
metastable state by a set of rate equations. The contributions to the rate equations include:

1. the intensity of the pumping (resonance) radiation,
2. excited state disorientation, and
3. metastable state spin relaxation.

For the more complicated case of optical pumping in $\text{He}^3$ discussed in the next section additional considerations must be included.

The rate at which the population densities change is given by

$$\frac{dn_i}{dt} = -\frac{1}{\tau_p} \sum_{k=1}^{K=9} B_{ik} n_i + \frac{1}{\tau_r} \sum_{j,k=1}^{j=3, K=9} B_{jk} A_{jk} n_j - \frac{1}{\tau_p} (n_i - \bar{n})$$

where

- $n_i =$ population density of the $i^{th}$ metastable sublevel
- $B_{ik} =$ probability for absorption connecting the $i^{th}$ metastable state to the $k^{th}$ excited state
- $A_{jk} =$ corresponding probability for spontaneous emission
- $\tau_p$ and $\tau_r =$ times characterizing the relaxation of the metastable atom due to the resonance light and collisional depolarization processes respectively.

The dependence of the $B_{ik}$ and $A_{jk}$ on the total angular momentum $J$ and its component $m$ along the axis of quantization is worked out in Condon and Shortley. The relative transition probabilities are shown in Table I.

The first term represents the absorption of light by the metastable atom. The second term represents the emission from the excited state and the return of the atom to the metastable state. The last term
TABLE I: Transition Probabilities $2^3S_1 \rightarrow 2^3P_J$ (He$^4$)

(a) Relative spontaneous transition probabilities
(b) Relative absorption probabilities for $\sigma^+$ radiation.

K is defined as the ratio of $I_0$ to $I_3$ light.
represents the rate at which the metastable atoms are thermalized by relaxation processes. The form of the second term can change if a disorienting collision takes place while the atom is in the excited state. If the mean time between atom-atom collisions approaches the excited state radiative lifetime, the spin of the $2^3P_J$ state is disoriented with respect to the orbital angular momentum and the metastable levels are repopulated at equal rates. In helium the excited state lifetime is $1.05 \times 10^{-7}$ sec and the pressure at which this "mixing" becomes significant is approximately 1 Torr.

In practice, the condition of the optical pumping process is observed by monitoring the transmitted light. Since the absorbed light depends on the level populations, any changes in the population ratios are reflected in the changing opacity of the sample. Further details of the optical pumping process in He and the solutions to the rate equations can be found in Refs. 12 and 16.

**D. Optical Pumping in He$_3$**

1. General considerations. Walters, Colegrove, and Scheerer subsequently extended the optical pumping process to He$_3$. In this case the circularly polarized resonance radiation again acts on the $2^3S_1$ metastable atoms but now the atoms possess a nuclear spin, $I = 1/2$. The energy levels are modified by the hyperfine interaction. The ground state buffer gas atoms are no longer magnetically inert and we must now inquire about the effect of collisions between the ground state atom and the metastable atom on the optical pumping process. The energy level diagram of the pertinent states of He$_3$ is shown in Fig. 2.

In a collision between a metastable and a ground state atom, there is a possibility that the 2s electron/the metastable atom and one of the
Fig. 2 Energy level diagram of the pertinent levels of $\text{He}^3$ in a weak magnetic field (not to scale).
electrons (1s) of the ground state atom will interchange spin coordinates. If the 2s electrons are polarized initially, the angular momentum can be transferred to the ground state atom and result in a polarization of the nuclear spin system. Wittke and Dicke\textsuperscript{19} and Purcell and Field\textsuperscript{20} first examined processes of this type for H-H collisions. Dehmelt wedded the spin-exchange theory and optical pumping in sodium vapor to the polarization of free electrons created by a brief electric spark in the absorption cell.\textsuperscript{10}

Briefly the exchange process between two atoms may be described as follows:

The spin wave function representing the stationary state of the molecule formed from atoms 1 and 2 is either symmetric or antisymmetric with respect to an interchange of spin coordinates. With each of these states there is associated a potential function which describes the interaction between the atoms. The two atom complex which results from a collision is described by mixtures of the symmetric and antisymmetric wave functions, and under the effect of the exchange potential one component advances in phase over the other leading to an interchange of the spin coordinates. The process can then be effective in changing the spin orientations of the colliding atoms. Angular momentum is conserved so that if the spin state of the metastable atom is changed by $\Delta M_f = -1$, the ground state atom must increase a corresponding amount.

In the following sections the optical pumping process in $\text{He}^3$ is discussed in detail.

The nuclear moments of the ground state ($^1S_o$) of $\text{He}^3$ ($I = 1/2$) can be polarized by means of spin exchange collisions with optically oriented
metastable atoms. The spin exchange occurs as a result of metastable ground state collisions:

\[ \text{He}^m(\text{I}) + \text{He}(\text{II}) \rightarrow \text{He}(\text{I}) + \text{He}^m(\text{II}) \]

This process where (I) and (II) denote the nuclear cores of the atoms is frequently referred to as metastability exchange. As in the case of \( ^4 \text{He} \), the higher \( M_f \) levels tend to become more highly populated at the expense of the others in the absence of strong thermal relaxation processes by the action of the circularly polarized resonance radiation. Now, however, metastability exchange collisions with the ground state atoms are an extremely effective source of metastable spin state relaxation.

2. Two level rate equations. One can examine in detail the results of the optical and collision induced transitions taking place by writing the rate equations for the appropriate metastable and ground state levels. No significant loss in generality occurs by reducing the system to a set of four levels: densities \( n_+ \) and \( n_- \) describing the metastable atoms and \( N_+ \) and \( N_- \) identifying the orientation of the ground state nuclear spins. Thus,

\[
\frac{dn_+}{dt} = \frac{n_+}{\tau_p} + \frac{n_-}{2\tau_R} - \frac{n_+}{2\tau_R} + \frac{N_+ n_-}{N\tau_2} - \frac{N_- n_+}{N\tau_2}
\]

where \( n_-/\tau_p \) is the rate at which the pumping light increases the population of the upper level, \( n_+/\tau_R \) is the rate at which \( n_\pm \) atoms are transferred to the \( n_\mp \) state by collisions with the walls and/or discharge products, and \( N_+ n_- / N\tau_2 \) is the rate at which \( n_\mp \) and \( N_\pm \) atoms exchange spins becoming \( n_\pm \) and \( N_\mp \) atoms. Similarly for the ground state system.
\[ \frac{dN_+}{dt} = \frac{N_-}{2T_R} - \frac{N_+}{2T_R} + \frac{n_+ N_-}{n T_2} - \frac{n_- N_+}{n T_2} \]  

where \( T_R^{-1} \) characterizes the rate of loss of angular momentum by the ground state while \( T_2^{-1} \) determines the rate at which ground state atoms undergo spin exchange collisions.

With the polarization for the metastable and ground states defined as

\[ p = \frac{n_+ - n_-}{n_+ + n_-} \quad \text{and} \quad P = \frac{N_+ - N_-}{N_+ + N_-} \]

the above rate equations become

\[ \frac{dp}{dt} = - \left[ \frac{1}{\tau_p} + \frac{1}{\tau_R} + \frac{1}{\tau_2} \right] p + \frac{P}{\tau_2} + \frac{1}{\tau_p} \]  

and

\[ \frac{dP}{dt} = - \left[ \frac{1}{\tau_R} + \frac{1}{\tau_2} \right] P + \frac{p}{\tau_2} \]  

where \( n_+ \) and \( n_- = n \) and \( N_+ + N_- = N \). \( T_2 \) and \( \tau_2 \) can be defined in terms of a common cross section for spin exchange and so we have the auxiliary condition that

\[ \frac{T_2}{\tau_2} = \left( \frac{\sigma v}{\langle v \rangle} \right) \frac{N}{n} \]

where \( V \) is the relative velocity of the colliding particles. The coupled
equations lead to the approximate solution
\[ p = Ae^{-t/T_p} + Be^{-t/T} + p_0 \]  \hspace{1cm} (7)

and
\[ p = \frac{\zeta}{\zeta} Ae^{-t/T_p} - \frac{B\zeta}{T^2} e^{-t/T} + p_0 \]  \hspace{1cm} (8)

for the condition that
\[ \zeta \ll T_2 \ll T_R \]

with
\[ \frac{1}{\zeta} = \frac{1}{\zeta_2} + \frac{1}{\zeta_R} + \frac{1}{\zeta_p} \]  \hspace{1cm} (9)

and
\[ \frac{1}{T_p} = \frac{\zeta}{T_2} \left( \frac{1}{\zeta_R} + \frac{1}{\zeta_p} \right) + \frac{1}{T_R} \]  \hspace{1cm} (10)

Since \( \tau \) is very much less than \( T_p \) the second term in Eqs. (7) and (8) decays rapidly so that \( T_p \) characterizes the approach of the polarization of both systems to equilibrium.

A phenomenological diagram describing the polarization and relaxation processes for the coupled system is shown in Fig. 3. This phenomenological approach defines and interrelates a set of characteristic times which describe the optical pumping process in He\(^3\). Consequently, by examining the properties of the optical pumping process (i.e., the interaction of the light beam with the metastable atoms and through this the interaction of the metastables with their surroundings) one can
Fig. 3 Schematic diagram indicating the interactions determining the polarizations of metastable and ground state $\text{He}^3$ atoms. Symbols are defined in the text.
acquire perhaps a greater understanding of the properties of the electrical discharge in helium insofar as these properties affect the pumping process.

3. Multilevel rate equations. It will be our purpose in this section to describe the optical pumping process in He$^3$ in terms of the properties of the actual multilevel system. The principal advantage offered by this approach over the more restricted description of the preceding section is that it relates the magnitude of the optical signal obtained by monitoring the transmitted light to the polarization of the sample. A disadvantage suffered by this approach is the added complexity.

Since He$^3$ possesses a nuclear spin $I = 1/2$, the levels are split as a result of the hyperfine interaction. Furthermore the existence of the spin exchange mechanism increases the complexity over the case for He$^4$. The rate equations for the system now involve eight nonlinear coupled differential equations. The difficulty in providing an analytic solution to the general time dependent populations is sufficiently difficult and the rewards sufficiently few to justify avoiding the time dependent solutions. The steady state solutions can be obtained exactly for several experimentally accessible conditions.

We will be able to show, however, from this limited analysis that the sample polarization can be observed and measured. We can then interpret the time dependence of the polarization process in terms of Eqs. (7) and (8) of the preceding section.

The rate equations for the population densities of the various levels can be written in terms of the matrix elements for electric dipole transitions between the $2^3S_1$ metastable states and the excited $2^3P_J$ levels and the coefficients for scattering into the various states
following a spin-exchange collision between a metastable and ground state atom. The rate of change of the population densities of the metastable level is of the form

\[
\frac{dn_i}{dt} = -\frac{n_i}{t_R} \sum_{j=1}^{j=6} A_{ij} n_j + \frac{l}{2} \sum_{j=1}^{j=6} \sum_{k=1}^{k=2} A_{jk} B_{ki} n_j n_k + \frac{l}{2} \sum_{j=1}^{j=6} C_{ij} n_j n_k - \frac{n_i}{t_2} \sum_{k=1}^{k=2} C_{ik} n_k - \frac{l}{2} (n_i - \frac{1}{2})
\]  

(11)

and for the ground state

\[
\frac{dN_i}{dt} = -\frac{N_i}{t_2} \sum_{j=1}^{j=6} C_{ij} n_j + \frac{l}{2} \sum_{j=1}^{j=6} \sum_{k=1}^{k=2} C_{jk} n_j n_k - (N_i - \frac{1}{2}) \frac{l}{t_R}
\]

(12)

where the levels are labeled according to the notation in Fig. 2.

The first term in Eq. (11) represents the change in the density of the \(i^{th}\) metastable state due to the absorption of a resonance photon. The \(A_{ij}\) are the relative probabilities for absorption. The second term represents the rate at which the \(n_i\) increase due to reemission. The \(B_{ki}\) are just the relative probabilities for the emission of a photon by an electric-dipole transition from the excited state \(k\) to the \(i^{th}\) metastable state. The third and fourth terms represent scattering out of and into the \(i^{th}\) metastable level due to spin-exchange collisions with atoms in the ground state. The final term represents the net loss of atoms from the \(i^{th}\) metastable state due to relaxation process not involving spin exchange.
The first two terms of Eq. (12) are the spin-exchange terms representing scattering out of and into the \( i \)th ground state. The last term represents losses not due to spin exchange. To conform to the notation in Ref. 18 we define the following terms:

1/\( \tau_p \) is proportional to the light intensity and represents the rate at which resonant photons induce transitions to the excited \( 3^3p_0 \) state,

1/\( \tau_R \) is the rate at which angular momentum is lost due to interactions of the metastable atoms with their surroundings. It does not include the effects of exchange collisions with the ground state,

1/\( \tau_2 \) is the frequency with which a metastable atom undergoes an exchange collision,

1/\( T_2 \) is the frequency with which a ground state atom participates in a spin-exchange collision with the metastable atoms, and

1/\( T_R \) is the rate at which angular momentum is lost as a result of interactions of the ground state atom with its surroundings exclusive of the effects of exchange collisions.

The times \( \tau_2 \) and \( T_2 \) can be related to a cross section for exchange collisions via: \( \tau_2 = (\sigma v n)^{-1} \) and \( T_2 = (\sigma v n)^{-1} \) where \( v \) is the relative velocity of the colliding atoms, \( N \) is the ground state density and \( n \) the metastable density. \( \tau_2 \) and \( T_2 \) are then related by the expression

\[
\tau_2 = n/N \cdot T_2.
\]

The spin-exchange process is discussed in detail in Appendix B and the scattering coefficients are calculated there. Table II contains the results of the computation of the coefficients. The \( C_{ij} \) are derived
\[
\begin{array}{cccccccccc}
\text{Out} & (1, 1) & (1, 2) & (2, 1) & (1, 5) & (1, 3) & (1, 6) & (2, 5) & (2, 2) & (2, 6) & (1, 4) & (2, 3) & (2, 4) \\
\text{In} & & & & & & & & & & & & \\
(1, 1) & 1 & & & & & & & & & & & \\
(1, 2) & & 13/18 & 3/18 & 2/18 & & & & & & & & \\
(2, 1) & & & 3/18 & 9/18 & 6/18 & & & & & & & \\
(1, 5) & & & & 2/18 & 6/18 & 10/18 & & & & & & \\
(1, 3) & & & & & 10/18 & 2/18 & 2/18 & 4/18 & & & \\
(1, 6) & & & & & & 2/18 & 13/18 & 1/18 & 2/18 & & \\
(2, 5) & & & & & & & 2/18 & 1/18 & 13/18 & 2/18 & \\
(2, 2) & & & & & & & & 4/18 & 2/18 & 2/18 & 10/18 \\
(2, 6) & & & & & & & & & 10/18 & 6/18 & 2/18 & 1/18 \\
(1, 4) & & & & & & & & & & 6/18 & 9/18 & 3/18 \\
(2, 3) & & & & & & & & & & & 2/18 & 3/18 & 13/18 \\
(2, 4) & & & & & & & & & & & & 1 \\
\end{array}
\]

\[(N_i, n_j) = (i, j)\]

**TABLE II: Scattering Coefficients for Spin Exchange**

The states of the incoming particles are shown in the column at the left. The states of the outgoing pair of particles are in the row at the top. The number at the intersection represents the probability that for the given incoming states the atoms will be scattered into a particular pair of outgoing states. Thus, if the two colliding atoms are initially in the states \(N_1\) and \(n_5\), the probability is 6/18 that the outgoing pair will be in the states \(N_2\) and \(n_1\).
from this table. The matrix elements for electric dipole transitions are evaluated in Condon-Shortley.\textsuperscript{13} If we assume the atom is in an eigenstate for which \( F, I, J, \) and \( M_f \) are good quantum numbers (i.e., at weak fields), we obtain for \( B_{ij} \) and \( A_{ij} \) the results shown in Table III.

We are now in a position to solve these equations under steady state conditions \( (n_i = 0) \) for several special conditions which are accessible experimentally. These will be:

1. the use of circularly polarized resonance light in which transitions to the \( 2^3P_0 \) level only are induced, and
2. complete mixing in the \( P \) states prior to reradiation
   (corresponding to gas pressures exceeding several Torr).

The qualitative features affecting the efficiency of the pumping process for the case in which transitions to excited states other than the \( 2^3P_0 \) state of \( \text{He}^3 \) are induced by the resonance radiation and the consequences of mixing vs no mixing are discussed in Ref. 18. Condition (1) is obtained experimentally by using a \( \text{He}^4 \) lamp to provide the resonance radiation. The isotope shift of approximately \( 1 \text{\AA}^2 \) is such that the light from this lamp does not induce transitions to the \( 2^3P_1 \) or \( 2^3P_2 \) state of the \( \text{He}^3 \) atom. Condition (2) occurs at gas pressures above 1 mm Hg. The rate equations under conditions (1) and (2) with spin exchange present reduce to the following eight equations

\[
\frac{dn_i}{dt} = \frac{\eta}{c_f} + \eta_0 \left( a + \frac{3N_i}{2} \frac{1}{18N} \right) + \eta_r \left( b + \frac{3N_i}{2} \frac{1}{18N} \right) + \eta_e \left( c + \frac{3N_i}{2} \frac{1}{18N} \right)
\]
\[
\frac{dn_e}{dt} = \frac{n}{6\zeta_R} + n_1 \left( \frac{a}{6\zeta_p} + \frac{3N_e}{18N \zeta_2} \right) + n_2 \left( \frac{-b + b}{\zeta_p} \frac{-d}{6\zeta_p} \right) + \frac{5N_1}{18N \zeta_2} - \frac{8N_e}{18N \zeta_2} \\
+ n_3 \frac{4N_1}{18N \zeta_2} + n_5 \left( \frac{c}{6\zeta_p} + \frac{2N_1}{18N \zeta_2} + \frac{2N_e}{18N \zeta_2} \right) + n_6 \frac{2N_1}{18N \zeta_2}
\]

\[
\frac{dn_o}{dt} = \frac{n}{6\zeta_R} + n_1 a + \left( \frac{b}{6\zeta_p} + \frac{4N_e}{18N \zeta_2} \right) n_2 + n_3 \left( -\frac{1}{\zeta_R} - \frac{5N_1}{18N \zeta_2} - \frac{8N_e}{18N \zeta_2} \right) \\
+ n_4 \frac{3N_1}{18N \zeta_2} + n_5 \left( \frac{c}{6\zeta_p} + \frac{2N_1}{18N \zeta_2} \right) + n_6 \left( \frac{2N_1}{18N \zeta_2} + \frac{2N_e}{18N \zeta_2} \right)
\]

\[
\frac{dn_a}{dt} = \frac{n}{6\zeta_R} + n_1 a \frac{n_2 b}{6\zeta_p} + n_3 \frac{3N_1}{18N \zeta_2} + n_4 \left( -\frac{1}{\zeta_R} - \frac{9N_1}{18N \zeta_2} \right) \\
+ n_5 \frac{c}{6\zeta_p} + n_6 \frac{6N_e}{18N \zeta_2}
\]
\[
\frac{dn_s}{dt} = \frac{n}{\tilde{\tau}_R} + n_i \left\{ \frac{a}{\tilde{\tau}_P} + \frac{6N_2}{18N_2} \right\} + n_e \left\{ \frac{b}{\tilde{\tau}_P} + \frac{2N_1}{18N_2} + \frac{2N_2}{18N_2} \right\} \\
+ n_s \frac{2N_1}{18N_2} + n_s \left\{ -\frac{c}{\tilde{\tau}_P} + \frac{c}{\tilde{\tau}_R} - \frac{8N_1}{18N_2} - \frac{5N_2}{18N_2} \right\} + \frac{n_eN_1}{18N_2}
\]

\[
\frac{dn_e}{dt} = \frac{n}{\tilde{\tau}_R} + \frac{n_in}{\tilde{\tau}_P} + n_s \left\{ \frac{b}{\tilde{\tau}_P} + \frac{2N_2}{18N_2} \right\} + n_e \left\{ \frac{2N_2}{18N_2} + \frac{2N_1}{18N_2} \right\} \\
+ n_s \frac{6N_1}{18N_2} + n_s \left\{ \frac{c}{\tilde{\tau}_P} + \frac{N_2}{18N_2} \right\} + n_e \left\{ -\frac{1}{\tilde{\tau}_R} - \frac{8N_2}{18N_2} - \frac{5N_1}{18N_2} \right\}
\]

\[
\frac{dN_i}{dt} = \frac{n}{2\tau_R} - \frac{N}{N} n \left\{ \frac{1}{\tilde{\tau}_R} + \frac{1}{18\tau_2} \left( 3n_2 + 6n_3 + 9n_4 + 6n_5 + 3n_6 \right) \right\} \\
+ \frac{N}{N} n \left\{ \frac{1}{18\tau_2} \left( 9n_1 + 6n_2 + 3n_3 + 3n_5 + 6n_6 \right) \right\}
\]

\[
\frac{dN_e}{dt} = \frac{n}{2\tau_R} - \frac{N_n}{N} \left\{ \frac{1}{\tilde{\tau}_R} + \frac{1}{18\tau_2} \left( 9n_1 + 6n_2 + 3n_3 + 3n_5 + 6n_6 \right) \right\} \\
+ \frac{N}{N} n \left\{ \frac{1}{18\tau_2} \left( 3n_2 + 6n_3 + 9n_4 + 6n_5 + 3n_6 \right) \right\}
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**TABLE III: Transition Probabilities** $2^3S_1 \rightarrow 2^3P_J$ (He$^3$, I = 1/2)  

- are relative absorption probabilities for $\sigma^+$ radiation from He$^4$ lamp.
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**TABLE III:** Transition Probabilities $2^3S_1 \rightarrow 2^3P_J$ (He$^3$, I = 1/2)

- are relative absorption probabilities for $\sigma^+$ radiation from He$^4$ lamp.
where \( a, b, \) and \( c \) are the probabilities for absorption of the resonance radiation out of the \( n_1, n_2, \) and \( n_5 \) levels respectively.

With the conditions implied by (1) and (2) above, the rate equations can be solved explicitly for the case in which the spin-exchange mechanism is the dominant relaxation mode present. The steady state solutions to the rate equations for this condition gives

\[
\frac{n_1}{n_2} = \frac{n_2}{n_3} = \frac{n_3}{n_4} = \frac{n_5}{n_6} = \frac{N_i}{N_2} = \frac{(1-P)}{(1+P)}
\]

and \( n_2 = n_5, n_3 = n_6. \) These relations lead to the results

\[
\begin{align*}
n_1 &= \left[ \frac{(1-P)^3}{(6+2P^2)} \right] n \\
n_2 &= n_5 = \left[ \frac{(1-P)^2(1+P)}{(6+2P^2)} \right] n \\
n_3 &= n_6 = \left[ \frac{(1-P)(1+P)}{(6+2P^2)} \right] n \\
n_4 &= \left[ \frac{(1+P)^3}{(6+2P^2)} \right] n
\end{align*}
\]

The function of the resonance radiation is to add angular momentum to the metastable spin system by increasing the populations of the states with the greatest \( M_f \) at the expense of the others. The spin-exchange process conserves angular momentum and serves merely to transfer polarization to the ground state. If the spin-exchange mechanism is the dominating
relaxation process, it can be shown (Appendix C) that the populations of the various metastable states are adjusted by collisions until the nuclear polarization of the metastable atoms is equal to the ground state polarization. Consequently, if we are to observe the polarization of the ground state by optical means, we must be able to observe the polarization of the metastable atoms.

A relationship between the light absorbed by the sample and the population densities of the absorbing levels can be simply obtained.

\[ I = \kappa \left[ an_1 + bn_2 + cn_s \right] \]  \hspace{1cm} (17)

In the absence of polarization the levels are essentially equally populated and the light absorbed is

\[ I_o = \kappa \left[ a+b+c \right] n/6 \]

The optical signal can be defined as the relative change in the absorbed resonance radiation as the sample goes from the polarized to the unpolarized condition. Thus,

\[ \frac{I_0 - I}{I_o} = \frac{6/n \left[ a(n/6-n_1)+b(n/6-n_2)+c(n/6-n_s) \right]}{a+b+c} \]  \hspace{1cm} (18)

When spin exchange is the dominating relaxation mechanism present, the populations of the \( n_i \) in terms of the nuclear polarization are given by Eq. (16). The optical signal then becomes

\[ \frac{I_0 - I}{I_o} = \frac{p}{3+p^2} \left[ 6-2p-3(1-p)^2 \left( \frac{b+c-a}{a+b+c} \right) \right] \]  \hspace{1cm} (19)
A knowledge of the quantities \(a\), \(b\), and \(c\) is sufficient to determine the nuclear polarization \(P\) in terms of the optical signal. These quantities in turn depend upon the relative probabilities for electric dipole transitions out of the \(n_1\), \(n_2\), and \(n_5\) levels respectively and the relative intensity of the resonance radiation exciting these transitions. If we define a parameter, \(f\), as the ratio of the intensity of the exciting radiation incident on the \(F = 3/2\) level to the total light intensity, Eq. (19) becomes

\[
\frac{I_o - I}{I_o} = \frac{P}{3 + P^2} \left[ 6 - 2P - 3(1-P) \frac{f(b-a-c)+c}{f(a+b-c)+c} \right]
\]

(20)

where the \(a\), \(b\), and \(c\) are now the square of the matrix elements for electric dipole transitions. If we assume \(L, S\) coupling for the \(3_p\) state, we find \(a\), \(b\), and \(c\) as given in Table IIIa. However, Colegrove, Schearer, and Walters\(^{18}\) calculate \(a = 0.41\), \(b = 0.15\), and \(c = 0.44\) on the basis of information contained in the work of Fred, \textit{et al.}\(^{21}\) in which a breakdown of the \(L, S\) coupling leads to a wave function of the excited state which is an admixture of the eigenfunctions for perfect \(L, S\) coupling. Equation (20) then becomes

\[
\frac{I_o - I}{I_o} = \frac{P}{3 + P^2} \left[ 6 - 2P - 3(1-P) \frac{4.4}{4.4 + 1.2f} \right]
\]

(21)
The quantity $f$, the relative illumination of the metastable hyperfine levels, is open to some question. The paper of Colegrove, Schearer, and Walters\textsuperscript{18} assumes that the levels are equally illuminated, i.e., $f = 0.5$. Greenhow\textsuperscript{23} has made some high resolution studies of the resonance line in absorption and concluded that no light falls on the $F = 1/2$ levels and hence that $f = 1$. However, the lamp linewidths quoted by Greenhow $\Delta \nu \sim 1.5 \text{cm}^{-1}$ are suspiciously small particularly in view of the high resolution tracing obtained by Colegrove\textsuperscript{24} for the resonance radiation from an $^4$He lamp operated under conditions similar to those employed in our experiments.

In many experiments involving scattering from a polarized $^3$He$^4$ target\textsuperscript{25} the polarization of the target needs to be accurately known ($\sim 1\%$). The uncertainty in $f$ can lead to errors approaching $20\%$.

Presently the only convenient method for measuring polarization under the conditions of a scattering experiment is by the optical method. Consequently, this question must be resolved. Fortunately a technique exists for obtaining, with some measure of confidence, the value of $f$. It is in essence an extremely high resolution spectroscopy method and yields a value of $f = 0.6$. The quantity $f$ can be determined by observing the relative strengths of the optical magnetic resonance signals of the $F = 3/2$ and $F = 1/2$ levels of the metastable state under the conditions in which the level populations are controlled by the exchange collisions and under the assumption that changes in the population of the $F = 3/2$ do not affect the $F = 1/2$ population (and conversely) during the time the observations are made. These conditions can be shown to be satisfied at a temperature of $77^\circ\text{K}$. The exchange cross section is still adequately large and the two optical signals are easily observed. The optical signal
due to the $F = 3/2$ levels is

$$
\Delta I_{3/2} = f_k \left[ a n_1 + b n_2 \right] - \frac{f_k}{4} \left[ (a+b) \left( n_1 + n_2 + n_3 + n_4 \right) \right]
$$

$$
= f_k \left[ a n_1 + b n_2 \right] - f_k \left[ (a+b) \frac{(1+P^2)}{2(3+P^2)} \right]
$$

while for the $F = 1/2$ level we have

$$
\Delta I_{1/2} = (1-f)kC n_3 - (1-f)kC \left[ \frac{(1-P^2)}{2(3+P^2)} \right]
$$

We have made use of the fact that while the spin-exchange process dominates so that Eq. (16) determines the populations densities, changes in the $F = 3/2$ level populations do not affect the $F = 1/2$ level densities in times shorter than $T_2$. These are the conditions present in the experiments of Colegrove, et al.\textsuperscript{26} Unpublished data taken at 77$^\circ$K (Fig. 4) gives the ratio of the two optical signals. Since

$$
\frac{\Delta I_{3/2}}{\Delta I_{1/2}} \sim \frac{3a+b}{c} \frac{f}{1-f}
$$

for small $P$ \hspace{1cm} (22)

we can calculate $f$ and find $f = 0.6$. The relationship between optical signal and polarization is then given by

$$
\frac{I_o - I}{I_o} = \frac{P}{3+P^2} \left[ 5.9 - 1.8P - 0.1P^2 \right]
$$

(23)
Fig. 4 Optical detection of the $F = 1/2$ and $F = 3/2$ resonances at 77°K.
The equation above is probably the best available representation of the polarization in terms of the optical signals. Lamp pressure and geometry might be expected to influence the results slightly but it is felt that the above equation represents the best available without a measurement made on these parameters at the same time as polarization measurements are made.

The relationship between nuclear polarization and the optical signal permits us to observe the dependence of the nuclear and metastable polarization on the characteristic times introduced in Sec. D.1. These relaxation times in turn are determined by the interactions of the metastable and ground state atoms with their surroundings.

The quantities which are directly accessible experimentally through the observation of the light transmitted through the cell (hence polarization) are $T_p$, $T_2^*$, $\tau_2$, and $T_R$. Quantities which can be adduced from Eqs. (10) and (16) also give us access to $\tau_R$ and $T_p^*$. The ground state density, $N$, is determined from a pressure measurement at the time of sample preparation while the metastable density, $n$, can be determined from the optical absorption or from the relation given by Eq. (6). The quantities $P_o$, $T_p$, and $T_R$ can also be determined by observing the nuclear magnetization by conventional NMR techniques. 27

It will be our purpose in the following sections to describe experiments which have been utilized to obtain measurements for each of these characteristic relaxation times and to determine their nature, i.e., the source of the relaxation.
III. Experimental Methods

A. Apparatus

The experimental apparatus required to optically polarize the He³ gas is shown in Fig. 5. The polarization of the sample can be monitored optically or by nuclear magnetic resonance techniques.

The source of resonance radiation at 1 µ is a capillary (4 mm i.d.) several inches in length filled to several Torr with reagent grade He⁴ gas. An attached reservoir reduces pressure loss due to diffusion of the He gas through the glass. A 50 Mc/sec oscillator operating at about 15 W output excites the lamp by capacitive coupling to the gas through external electrodes. The resonance radiation from the lamp is first linearly polarized and then passed through a quarter wave plate consisting of a 1 mil cellophane sheet.

The absorption cells were usually constructed of pyrex spheres 5 cm in diam and filled with high purity He³ gas to pressures from 0.2 to 20 mm Hg. An elaborate cleaning process is usually required to provide satisfactory cells (see Ref. 18).

A low powered oscillator at 50 Mc/sec or 500 kHz supplies the power to excite a small fraction of the ground state He³ atoms in the absorption cell to the metastable state. Again external electrodes are used. Internal electrodes can be used but they are extremely microphonic and tend to getter the He over long periods. The rf magnetic field from the excitation is sufficiently large to saturate the spin systems so that the frequency of the excitation oscillator must be well away from the larmor frequencies of the metastable or ground state atoms.

The polarization of the sample can be observed by monitoring the transmitted resonant radiation. A PbS cell detects the light passing
Fig. 5 Schematic of equipment used in performing resonance experiments on optically pumped He$^3$. 
through the absorption cell. Small circular coils are available for providing an oscillatory magnetic field at the larmor frequency of the metastable or ground state atom.

Nuclear resonance experiments utilized an Anderson bridge at 800 kHz. The output of the bridge was detected with a National HR0-60 Receiver and the output displayed on a Mosely X-Y Recorder.

The magnetic environment of the sample was controlled by the use of a highly homogeneous solenoid and Helmholtz coils. The optical pumping process can be performed in any field in which the field direction is well defined with respect to the direction of the polarized resonance radiation. The effectiveness of the circularly polarized resonance radiation in inducing changes $\Delta M_F = +1$ (or -1) in $\langle F_z \rangle$ on absorption (where $z$ is the axis of the magnetic field) is a maximum when the optic and magnetic axes are collinear.

**B. Experimental Techniques**

The time constants defined earlier can be determined by observing the response of the polarization (hence, transmitted light) to a variety of perturbations imposed on the system.

1. **Polarization.** Equation (23) relates the optical signal to the polarization of the nuclear spin system. The optical signal is obtained by monitoring the change in the transmitted light from the pumped to the unpumped condition. The transmitted light is proportional to the voltage developed across the PbS detector. The transmitted light is first measured when the sample is pumped. An oscillatory magnetic field at the resonant frequency of the nuclear spin system equalizes the populations (i.e., forces spin temperature to infinity). The strong spin-exchange relaxation then forces the metastable spin temperature to
infinity and the light now reaching the detector remeasured obtaining \( I_2 \). The discharge is turned off and the incident light \( I_0 \) measured. The optical signal is then

\[
\frac{I_2 - I_1}{I_0 - I_2} = \frac{\Delta I}{I} = S_{\text{opt}}
\]

A second useful optical technique consists of measuring the change in the intensity of the transmitted light as the external dc magnetic field is adiabatically reversed. The sample magnetization follows the applied magnetic field; the direction of the resonance radiation remaining fixed. The adiabatic reversal must be completed in a time short compared to the time required to polarize the sample, \( T_p \). Advantages of this method are that the optical signal is twice as large as that obtained by the first method for a given polarization and since the sample magnetization is not destroyed, the measurement can be made repetitively. In the first method the saturating rf magnetic field destroys the sample magnetization and the system must be repumped before the measurement can be repeated. In both techniques care must be exercised to insure that the application of the changing fields does not produce changes in the discharge level which could result in spurious contributions to the optical signal.

The measurement of the polarization can also be made using conventional NMR techniques. The use of this method to measure the \( \text{He}^3 \) polarization is discussed in detail in Appendix D. The advantages of this method is that the sample magnetization is measured directly and
does not depend upon a derived relationship between light absorbed and level populations. The magnetization of a water sample is then used to obtain an absolute measure of polarization which is independent of the details of the optical pumping process.

2. \( T_p \): Polarization pumping time. Equations (7) and (8) give the time dependence of the polarization. Since the time constant for the second term is very short, \( T_p \) characterizes the approach of the polarization to equilibrium. The light transmitted is monitored as the sample polarization increases from zero to \( P_o \) (or conversely the decay of the polarization could be monitored). The equilibrium polarization is approached exponentially with a time constant given by \( T_p \). In practice, however, it is usually inconvenient to continuously observe the transmitted light since the detector drift can obscure the measurement particularly for some of the longer \( T_p \). Measurements of \( T_p \) were obtained by observing the light level at the detector at \( t = 0 \) and \( P = 0 \). Then after a time \( t = t_1 \) the levels are saturated by an oscillatory magnetic field at the larmor frequency of the ground state nuclear spins and the light intensity change measured. Since \( \Delta I \propto P \) for small \( P \), we can then plot \( P \) vs the time \( t \) for various \( t_1 \) and extract the time constant \( T_p \).

3. \( T_{2\perp}, T_2 \): Exchange times. Collisions between atoms in which angular momentum is transferred are an important relaxation mechanism. \( (T_2)\) has been used to characterize the frequency with which a metastable atom undergoes an exchange collision with the reservoir of ground state atoms. \( (T_2)^{-1} \) is the rate for the inverse process.

The cross section, \( \sigma \), for exchange and its temperature dependence was obtained experimentally by Colegrove, Walters, and Schearer.\(^{26} \) A
knowledge of the ground state and metastable densities are then sufficient to determine $T_2$ and $\tau_2$. Techniques for directly observing $T_2$ and $\tau_2$ are discussed in Refs. 18, 23, 26, and 30. These methods are discussed in Appendix E.

4. n: Metastable density. The metastable density for a given light intensity, determines the amount of angular momentum that can be added to the system per second. Subsequent losses involving the metastable atom help to determine the attainable polarization. This density can also be used to describe the "intensity" of the discharge if we can relate other discharge characteristics to it. Consequently a knowledge of the metastable density as a function of the other observables in the system can be extremely revealing.

The simplest way in which we can determine the metastable density is by way of the optical absorption of the resonance radiation by the atoms.31 The absolute values of the metastable density obtained by the use of high/optical techniques can be quite good (≈ 1%) if the appropriate precautions are taken. However, the conditions under which these optical pumping experiments are conducted is not amenable to this high precision. Greenhow23 has addressed himself to this point and obtains densities with an accuracy on the order of ± 20%. High resolution optical equipment was not available to us and the relation between percent absorption and metastable density may be in error by a factor of two or more. The relative density as a function of percent absorption is probably much more reliable.

5. $T_R$, $\tau_p$, $T_R$: Relaxation time measurements. The quantities $T_R$, $\tau_p$, and $T_R$ cannot be measured directly in He$^3$ since the spin-exchange mechanism dominates relaxation processes and in general masks the effects
of the other relaxation times. In an effort to observe any effects of these parameters on the pumping process, experimental conditions were varied. The dependence of the polarization on the intensity and character of the pumping light was observed. Experiments were also conducted in which the discharge intensity was modulated and the optical signal monitored. The metastable pumping time \( \tau^P \) and the metastable relaxation time \( \tau_R \) have been measured by Byerly\(^{16} \) in the case of He\(^4 \). The processes leading to metastable relaxation are the same in He\(^3 \) as in He\(^4 \). The pumping time in He\(^3 \) can be expected to be different since \( \tau^P \) also depends on the efficiency of the pumping process.

The nuclear spin-lattice relaxation time in He\(^3 \) in the absence of the discharge is discussed in Part II.
IV. Experimental Results and Discussion

There are three quantities which represent the interaction the spin systems of the metastable and ground state of He\(^3\) with their surroundings. \(\tau_p\) represents the interaction of the resonance radiation with the metastable atoms and \(\tau_R\) represents relaxation process related to various interactions of the metastable atoms with the atomic and molecular constituents in the electrical discharge. \(\tau_R\) is determined by ground state relaxation processes involving the constituents of the electrical discharge other than \(2^3S_1\) metastable atoms. As pointed out earlier these quantities are inaccessible directly by experiment. However, with the aid of the theory developed in Part II and the experimental measurements of the polarization, \(P\), and the pumping time, \(T_p\), reasonable values for these relaxation times can be obtained.

It will be our purpose in the following paragraphs to discuss separately these relaxation times and on the basis of known gaseous reactions which occur in electrical discharges in He describe various interactions which can lead to these relaxation processes.

A. \(\tau_p\), \(T_p\): Pumping Times

The quantity \(\tau_p\) is a measure of the effectiveness of a given light intensity in inducing an absorption-emission cycle which leaves behind a unit of angular momentum, i.e., \(\Delta M_F = +1\) of the metastable atom. The intensity of the circularly polarized resonance radiation is proportional to \(\tau_p^{-1}\). A He\(^4\) source of radiation has been found to be superior at all but the lowest sample pressures to a He\(^3\) lamp in producing large orientations of the spins. Figure 6 compares the high resolution spectra of both a He\(^3\) and He\(^4\) lamp at 10830 Å.\(^2\) Although an absorption cell containing He\(^3\) will absorb approximately eight times as much light for
Fig. 6 Structure and isotope shift for the $^2S - ^2P$ spectral line of helium (10 830 Å) from Fred, et al. 21
illumination with He$^3$ as for He$^4$, the use of a He$^3$ lamp is relatively ineffective in producing polarization at pressures greater than 1 Torr. If the resonance radiation is capable of inducing transitions to the $2^3P_0$, $2^3P_1$, and $2^3P_2$ levels as is the case when a He$^3$ lamp is used, P-state mixing as discussed in Sec. II.D dramatically reduces the polarization obtainable.

The isotope shift in He is such that a He$^4$ lamp induces transitions to the $2^3P_0$ levels in He$^3$ only; consequently, mixing does not deteriorate the optical pumping process. Figure 12 in the paper by Colegrove, et al.18 illustrates the effect.

The quantity $\tau_p$ cannot conveniently be measured directly in He$^3$ optical pumping although measurements conducted at liquid helium temperatures of the type utilized by Byerly16 in He$^4$ might be useful. $\tau_p$ can be obtained from measurements of the polarization as of function of $T_p$ and $n/N$. The steady state solutions to the polarization Eqs. (4) and (5) lead to the equilibrium polarization of the system in terms of the characteristic relaxation times. Thus,

$$P_0 = \frac{1}{\tau_p} \left[ \left( \frac{1}{\tau_p} + \frac{1}{\tau_R} \right) + \frac{T_2}{\tau_2} \left( \frac{1}{T_R} \right) \right]^{-1}$$

(24)

and $P_0 = p_0$ assuming $T_R \gg T_2$, a condition which is always found to be true experimentally. Substitution of Eq. (10) into the above leads to

$$P_0 = \frac{1}{\tau_p} \left( \frac{n}{N} T_p \right)$$

(25)

A plot of $P_0$ vs $(n/N)T_p$ is a straight line with slope $(\tau_p)^{-1}$. The metastable density is obtained from absorption measurements and the ground
state density is obtained from pressure measurements at the time of sample preparation. The results of a plot of polarization is \( \frac{n}{N} T_p \) are shown in Fig. 7. The slope gives a value of \( T_p \approx 4 \times 10^{-4} \) sec for our lamps under the conditions described earlier. All the measurements utilized the same lamp operating at the same excitation level. The two curves shown are for two different excitation frequencies of the electrical discharge. The difference in the two curves probably results from nonuniformities in the discharge over the sample cell. Figure 8 is a plot of the metastable density in He\(^3\) as a function of the percentage of light absorbed from a He\(^4\) lamp. The curve is obtained from a knowledge of the emission and absorption line widths and the oscillator strengths. The dependence of the polarization as a function of metastable density for various pressures is illustrated in Figs. 9 - 12.

The quantity \( T_p \) is obtained by monitoring the polarization as a function of time as shown in Fig. 13. \( T_p \) is typically on the order of tens of seconds.

One other aspect of the spectral distribution of the resonance radiation and its relation to the polarization produced in the He\(^3\) gas by optical pumping was investigated experimentally. The metastable density was maintained at a constant level as was the intensity of the 1 \( \mu \) resonance radiation from a capillary lamp. As the lamp pressure was varied between 1 and 10 mm Hg the percent absorption varied as well as the obtainable polarization. Table IV summarizes the observations.

These results can be explained satisfactorily on the basis of spectrometer recordings made with a 0.5 meter Jarrel Ash spectrometer of the 1 \( \mu \) resonance radiation as a function of lamp pressure. The ratio of the light intensity at the absorption frequency to the total intensity at
Fig. 7 Polarization of He$^3$ at 2.6 mm Hg produced by a constant intensity pumping lamp for different metastable concentrations. The two lines represent discharge excitation at 50 Mc and 500 kc. The slope of the curve $P_o$ vs $(n/N)T_p$ yields the metastable pumping time $T_p$. 
Fig. 8 Percent absorption vs metastable density. The left scale is absorption of the light from a He³ cell and the right scale for a He⁴ lamp.
Fig. 10 Polarization vs percent absorption. Pumping light is held constant.
Fig. 11 Polarization vs percent absorption. Pumping light is held constant.
Fig. 12 He\(^3\) polarization as a function of sample pressure in mm Hg. Pumping light held constant. This curve is extracted from the data of Figs. 9 - 11. 500 kHz excitation.
Fig. 13 Growth of polarization as a function of time. The high frequency discharge produces a higher polarization than the 500 kc excitation. The resultant polarizations at the two frequencies is approximately in the ratio of the pumping times.
<table>
<thead>
<tr>
<th>Lamp</th>
<th>Pressure</th>
<th>Relative Polarization</th>
<th>Relative Total Intensity</th>
<th>Relative Pump Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>He⁴</td>
<td>15 mm Hg</td>
<td>36</td>
<td>37</td>
<td>29</td>
</tr>
<tr>
<td>He⁴</td>
<td>7 mm Hg</td>
<td>34</td>
<td>44</td>
<td>30</td>
</tr>
<tr>
<td>He⁴</td>
<td>3 mm Hg</td>
<td>30</td>
<td>39</td>
<td>26</td>
</tr>
<tr>
<td>He⁴</td>
<td>1 mm Hg</td>
<td>25</td>
<td>33</td>
<td>22</td>
</tr>
<tr>
<td>He³</td>
<td>3 mm Hg</td>
<td>20</td>
<td>39</td>
<td>39</td>
</tr>
</tbody>
</table>

Sample Pressure ~ 2.6 mm Hg

**TABLE IV:** The total intensity of the 1 μ resonance radiation peaks between 4 and 8 mm lamp pressure. The polarization produced, however, peaks at a higher pressure because the useful pumping intensity from a He⁴ lamp continues to increase at the expense of light components which are not utilized. A He³ lamp, while providing a high intensity at the absorbing lines, produces relatively little nuclear polarization as a result of P state mixing.
1 µ varies in the same manner as the percent of absorption. Figure 14 shows the spectral lines at 10 mm Hg and 1.5 mm Hg lamp pressure respectively.

B. $\tau_R$: Metastable Relaxation

The characteristic time $\tau_R$ is a measure of the relaxation processes associated with losses of angular momentum from the metastable spin system not including exchange mechanisms. $\tau_R$ cannot be observed directly in He$^3$ optical pumping in the case for which the exchange mechanism dominates. One can observe $\tau_R$ directly at liquid helium temperature in low pressure samples of He$^3$ or alternately one can observe $\tau_R$ in He$^4$ where the exchange mechanism cannot relax the He$^4$ metastable atoms. The relaxation processes affecting $\tau_R$ are identical in the two systems. The presence of a nuclear spin serves only to introduce a relaxation due to the exchange mechanism which is included with $\tau_2$.

The measurement of $\tau_R$ in He$^4$ is considerably simpler than the similar measurement in He$^3$. $\tau_R$ can be observed by measuring the metastable resonance linewidth which in He$^4$ occurs at $g = 2(2.8 \text{ Mc/sec } G^{-1})$. Byerly$^{16}$ measured $\tau_R$ in He$^4$ by monitoring the buildup of the optical signal after a saturating rf field was suddenly removed. The optical signal increases exponentially at a rate given by $1/\tau_R + 1/\tau_P$. An extrapolation to zero light intensity ($\tau_P \to \infty$) yielded a measurement of $\tau_R$. His results at 0.2 mm and 1 mm sample pressures are reproduced in Fig. 15.

An upper limit can be placed on the magnitude of $\tau_R$ from other types of experiments. For example, the decay of the metastable atoms due to diffusion and three body collisions in the afterglow of the discharge can be observed by monitoring the decay of the absorbed light after the
Fig. 14 Spectra of He$^3$ lamps obtained with a 0.5 meter Jarrel-Ash spectrometer comparing two different lamp pressures. The radiation is at 10 830 Å.
Fig. 15 Metastable relaxation rate as a function of metastable density in He$^4$ discharge. After Byerly.16
discharge excitation is removed in the manner pioneered by Phelps and Molnar.\textsuperscript{32} The metastable density decays according to the relation

\[
\frac{\partial n}{\partial t} = D_n \nabla^2 n - \alpha n
\]

where \(D_n\) is the diffusion coefficient and \(\alpha\) is the three body rate coefficient at a pressure \(p\). The decay time as a function of cell pressure is measured for He\textsuperscript{3} metastables and is shown in Fig. 16. The diffusion coefficient obtained in this way is \(D_n = 600 \text{ cm}^2 \text{ sec}^{-1} \text{ mm Hg}^{-1}\). The decay of the absorbed light as the discharge level is reduced but not extinguished was also investigated to determine the effect of the discharge on metastable lifetimes. The results are shown in Figs. 17 and 18, and indicate that relaxation of this type depends linearly on the residual metastable density and extrapolates at vanishing metastable density to the lifetimes measured when the discharge is absent.

These latter measurements obtained by monitoring the decay of the absorbed light are sensitive only to that part of \(\tau_R\) which results from the loss of a metastable atom from the system (e.g., diffusion to the walls or conversion to the singlet state). The \(\tau_R\) appearing in the polarization equation, however, also includes the effects of relaxation between the triplet metastable magnetic sublevels. The measurements of Byerly\textsuperscript{16} were sensitive to this relaxation process as well. The measurements shown in Figs. 17 and 18 lead to the conclusion that the metastable lifetime depends upon the discharge intensity (as measured by the metastable density) in a linear manner and extrapolates to the Phelps and Molnar\textsuperscript{32} times as the metastable density is reduced. Consequently, we obtain an upper limit on \(\tau_R\) at zero discharge level (limit of \(n = 0\)) is given by Fig. 16 and that the relaxation rate increases
Fig. 16 $^3$He metastable relaxation time in the afterglow vs sample pressure. The dotted line represents losses due to three body collisions.
Fig. 17 Decay of He\textsuperscript{3} metastables as the discharge level is decreased suddenly. Sample pressure was 1.0 mm Hg. The three curves represent different residual metastable densities.
Fig. 18 Relaxation rate of metastable density vs residual density for several pressures. The discharge level is suddenly decreased from an initial value to the final value n.
linearly with \( n \) with the same slope for all pressures in the presence of
the discharge.

\( \tau_R \) losses in the afterglow of the discharge are discussed in the
paper by Burhop.\(^{33} \) To summarize we have for \( \tau_R \) processes the following
possibilities:

(1) diffusion to the walls,

(2) three body collisions,

(3) metastable-metastable, and

(4) metastable-ground state collisions (spin-orbit coupling).

We list here the gaseous\(^{34} \) reactions in which the metastable atom
can participate in the afterglow. For comparison purposes the density
of the ground state atoms will be taken as \( 9 \times 10^{16} \text{ cm}^{-3} \) (2.6 Torr) and
the density in a typical discharge \( 2 \times 10^{10} \text{ cm}^{-3} \) for the triplet
metastable atoms (corresponding to 2.6% absorption of the light from a
\( \text{He}^4 \) lamp). The contribution to \( \tau_R \) is calculated where possible and
estimated elsewhere for processes at room temperature.

(1) \( \text{He}^M \rightarrow \text{walls by diffusion}. \) The diffusion coefficient for
\( \text{He}^2 \) we have measured as \( D_n = 600 \text{ cm}^2/\text{sec}^{-1} \). The diffusion
length \( \Lambda \) for a spherical cell of radius \( R \) is given by
\( R/\pi \) and the diffusion time is measured to be 1.4 msec for the
lowest diffusion mode.

(2) \( \text{He}^M + 2\text{He} \rightarrow \text{He}^M \frac{3}{2} \Sigma_g^+ + \text{He} \) (three body collisions).
\( \text{He}^M \frac{3}{2} \Sigma_g^+ \rightarrow 2\text{He} + h\nu \) (collision induced radiation).
\( \sigma = 3 \times 10^{-23} \text{ p cm}^2 \) (p in Torr).
\( \tau = 0.70 \text{ sec} \).

(3) \( \text{He}^M + \text{He}^M \rightarrow \text{He}^+ + \text{He} + e \).
\( \sigma = 10^{-14} \text{ cm}^2 \).
\( \tau = 25 \text{ msec.} \)

(4) \( \text{He}^M + \text{He} \rightarrow 2\text{He}. \)
\[ \sigma = 10^{-21} \text{ cm}^2. \]
\( \tau = 60 \text{ msec.} \)

(5) \( \text{He}^M + \text{impurities} \rightarrow (\text{impurity})^+ + e. \)
\[ \sigma(\text{argon}) = 6.6 \times 10^{-16} \text{ cm}^2. \]
\[ \sigma(\text{N}_2) = 6.4 \times 10^{-16} \text{ cm}^2. \]
\[ \sigma(\text{H}_2) = 6.0 \times 10^{-16} \text{ cm}^2. \]
\[ \sigma(\text{Ne}) = .28 \times 10^{-16} \text{ cm}^2. \]
\[ \sigma(\text{kr}) = 1 \times 10^{-16} \text{ cm}^2. \]

Since the impurity density is always less than 1 ppm then \( \tau > 100 \text{ msec.} \)

Process (4) represents a loss of metastable atoms as a result of spin-orbit coupling in \( ^2S_1 - ^1S_0 \) collisions. This mechanism was considered by Biondi\(^{35}\) who assigned a cross section \( \sigma = 10^{-21} \text{ cm}^2 \) for the reaction although this was subsequently shown to be in error by Phelps and Molnar.\(^{32}\) Watt and Jaspar\(^{36}\) have also suggested a spin-orbit coupling as a possible \( \tau_R \) process.

Spin-orbit coupling requires a term in the interaction Hamiltonian of form \( \alpha \mathbf{L} \cdot \mathbf{S} \). To first order, in elastic collisions between \( S \)-state atoms, \( \mathbf{L} = 0 \) and there can be no spin-orbit term. In higher order, during the collision, the atoms may be distorted corresponding to an admixture of higher atomic states. This should be a very small effect for both \( ^2S_1 \) and \( ^1S_0 \) because the admixture is proportional to the reciprocal of the energy separation to the nearest state with \( \mathbf{L} \neq 0 \) - i.e., \( 1 \text{ eV} \) for \( ^2S_1 \) and about \( 21 \text{ eV} \) for \( ^1S_0 \).

Thus, in the afterglow the primary contribution to the metastable relaxation rate is wall diffusion. However, since the three body
collision cross section is pressure dependent it can become the dominant loss mechanism at high pressures, the point at which it enters being determined by the sample diffusion length. With a 65 cm\(^3\) sample this point is about 10 mm Hg.

The five processes discussed above all involve the loss of metastable atoms. Angular momentum can also be lost if the metastable atom merely undergoes a change in its spin state. Processes of this type are as follows.

\[
(6) \quad \text{He}^\uparrow \downarrow + e(\downarrow) \rightarrow \text{He}^\uparrow \downarrow + e(\downarrow) \text{ by spin exchange.}
\]
\[
e(\downarrow) \rightarrow \text{walls by ambipolar diffusion. The exchange frequency is } \langle \tau \rangle^{-1} = \nu \sigma n_e. \text{ For } n_e \sim 10^9 \text{ cm}^{-3} \text{ and } \sigma v \sim 10^{-7} \text{ cm}^3 \text{ sec}^{-1} \text{ (estimated) we find } \tau \approx 10 \text{ msec, a time comparable to the diffusion rate. Thus, spin exchange with free electrons in the afterglow can contribute to polarization loss in the metastable system.}
\]

In the presence of the discharge there are several additional reactions which can take place.

\[
(7) \quad \text{He}^\uparrow (T) + e \rightarrow \text{He}^\uparrow (S) + e \text{ (singlet-triplet conversion).}
\]
\[
(8) \quad \text{He}^\uparrow (T) + e \rightarrow \text{He}^+ + 2e.
\]
\[
(9) \quad \text{He}^\uparrow (T) + e \rightarrow \text{He}^\uparrow' + e \text{ and } \text{He}^\uparrow' \rightarrow \text{He}^\uparrow + e.
\]

Process (7) cannot occur in the afterglow because of the energy defect of 0.8 eV required to produce the singlet. The first two processes here represent a loss of metastable atoms from the system. The experiment described earlier in which the discharge level was changed (but not extinguished) and the metastable density monitored is sensitive only to metastable loss. The experiment performed by Byerly\(^{16}\) includes losses from all the sources considered and is a direct measure of the metastable
spin relaxation time $\tau_R$. This measured time with discharge on is always shorter than the corresponding quantity with discharge extinguished. Consequently, processes (1) - (5) above can be eliminated as the primary source of relaxation.

Byerly attributed the loss mechanism to $^4\text{He}^M$ collisions with the hot electrons of the discharge. The loss rate is given by $(\tau^{-1}) = \sigma v n$ and $= (2 \times 10^{-14}) \times (6 \times 10^7) \times n_e$ leading to $\tau \sim 1$ msec for $n_e = 8 \times 10^8$ electrons cm$^{-3}$ in the discharge, an entirely reasonable result. Reaction (6) above yields a spin exchange time of the same magnitude if $\sigma v$ is taken to be $10^{-6}$ to $10^{-7}$ cm$^3$ sec$^{-1}$ for hot electrons. However, the polarization acquired by the hot electrons (3 eV) is necessarily small. The ambipolar diffusion rate of electrons in the presence of the electrical discharge leads to an electron lifetime on the order of $10^{-5}$ sec. Since the exchange time is $10^{-3} - 10^2$ sec the electron polarization can be no greater than .01 to .001 of the metastable polarization; thus, each exchange collision is in effect a depolarization collision for the metastable atom. Attempts to observe the electron resonance have been unsuccessful because of this low polarization.

C. $\tau_r$: Ground State Relaxation

Losses of angular momentum by the ground state spin systems are represented by the characteristic time $\tau_r$. The properties of the ground state relaxation have been investigated for several different environmental conditions:

(1) when the discharge is present $\tau_r$ processes are dominated by depolarization collisions of the ground state $^3\text{He}$ atoms
with atomic and molecular species created by the discharge,

(2) when the discharge is absent the relaxation is controlled by surface effects of the containing vessel, and

(3) when inhomogeneities in the applied magnetic field are present the Brownian motion of the spins can result in a depolarization of the sample.

The discussion of conditions (2) and (3) is deferred to Part II of this thesis.

Loss mechanism in the ground state spin system cannot be measured directly, again because the spin-exchange process masks observations. An upper limit on \( T_R \) can be established by observing the decay of the nuclear polarization in the absence of the discharge (i.e., when spin exchange is absent) by conventional NMR. The \( T_R \) obtained in this way is significantly longer (> 1 hr) than \( T_R \) obtained in the presence of the discharge indicating that the ground state atom is influenced by the discharge.

The influence of the discharge on the ground state relaxation can be obtained indirectly from measurements of \( T_p, \tau_p, T_R, \) and \( P_0 \). From Eq. (24) we have

\[
P_0 = \frac{1}{\tau_p} \left[ \left( \frac{1}{\tau_p} + \frac{1}{\tau_R} \right) + \frac{T_2}{\tau_2} \frac{1}{T_R} \right]^{-1}
\]

With the exception of \( T_R \) all the quantities in the above equation are accessible experimentally. Thus we can use this equation to deduce \( T_R \). We note first that if \( T_R \) is very long, so that the last term in the
square bracket can be neglected, the polarization becomes

\[ P = \frac{\tau_R}{\tau_R + \tau_P} \]

Using the value of \( \tau_p (4 \times 10^{-4} \text{ sec}) \) obtained for our lamps under the conditions described earlier from the results of Fig. 7 and typical values of \( \tau_R (10^{-3} \text{ sec}) \) represented by Fig. 15 we obtain \( P \approx 0.70 \). Since the measured values of \( P_o \) are well below this (\( P_o \sim 0.10 \)) evidently the polarization is being seriously degraded by losses due to \( T_R \) processes. Thus,

\[ \frac{T_R}{\tau_R} \frac{1}{\tau_R} > \left( \frac{1}{\tau_R} + \frac{1}{\tau_P} \right) \]

It is also observed that the polarization is directly proportional to the pumping light intensity, i.e., to \( \tau_p^{-1} \). This implies that the \( 1/\tau_p \) term in the square bracket of Eq. (24) above must be small compared to one of the other two terms. Since experimental measurements indicate that \( \tau_p < \tau_R \), we are forced to the conclusion that \( n/\tau_R < N/\tau_R \), i.e., relaxation losses in the ground state are greater than those in the metastable state. A substitution of typical values in Eq. (24) also leads to this conclusion. For example, at 2.6 mm with the sample cell absorbing 2\% of the 1 \( \mu \) radiation from a He \( \lambda_4 \) lamp we measure

\[ \begin{align*}
T_p &= 150 \text{ sec} \\
n &= 1.6 \times 10^{10} \text{ cm}^{-3} \\
N &= 8.3 \times 10^{16} \text{ cm}^{-3} \\
P_o &= 0.056 \\
\tau_p &\sim 4 \times 10^{-4} \text{ sec} \\
\tau_R &\sim 10^{-3} \text{ sec}
\end{align*} \]

and find \( T_R \sim T_p = 150 \text{ sec} \).

This value of \( T_R \) is to be compared with the ground state spin relaxation obtained in the absence of the discharge, viz: \( T_R \sim 3600 \text{ sec} \) or more. Consequently, we conclude that (a) the primary source of
angular momentum loss involves the ground state atoms, and (b) interactions with the discharge provide the loss mechanism.

It is now our purpose to examine various depolarization processes involving collisions of ground state atoms with the species created by the presence of the electrical discharge. We will consider the following processes and attempt to determine the relative importance of them in leading to the observed relaxation:

1. resonant charge transfer between a ground state atom and the atomic ion
   \[ \text{He}(\uparrow) + \text{He}^+(\downarrow) \rightarrow \text{He}^+(\uparrow) + \text{He}(\downarrow) \]
   followed by ambipolar diffusion of the atomic ion to the walls where recombination takes place,

2. exciting (or ionizing) collisions between hot (> 20 eV) electrons and ground state atoms
   \[ \text{He} + e \rightarrow \text{He}' + e \text{ or } \rightarrow \text{He}^+ + 2e, \]

3. collisions between the metastable molecule and the ground state atom in which the atom physically exchanges with one of the atoms in the metastable molecule
   \[ \text{He}_2(3\Sigma_g^+) + \text{He}(\uparrow) \rightarrow \text{He}_2(3\Sigma_g^+) + \text{He}(\downarrow), \]
   and

4. atom-atom interchange collisions between the molecular ion and the ground state atom
   \[ \text{He}(\uparrow) + \text{He}_2^+ \rightarrow \text{He}(\downarrow) + \text{He}_2^+. \]

**Process (1).** \( \text{He}(\uparrow) + \text{He}^+(\downarrow) \rightarrow \text{He}^+(\uparrow) + \text{He}(\downarrow) \). A symmetric charge transfer of this type has a large probability of occurrence. The cross section for this process is \( \sigma_T \sim 10^{-15} \text{ cm}^2 \). McDaniel\(^{38}\) summarizes the experimental results obtained for \( \sigma_T \) at ion energies greater than 2 eV. At low energies the cross section is derived from measurements on the
mobility of the He$^+$ in the parent gas. Quantum mechanical calculations of the mobility of ions in their parent gas have been made. The usual calculation includes interactions involving (a) rigid sphere repulsion, (b) polarization attraction, and (c) symmetry forces. The symmetry forces include resonance attraction and repulsion and resonant charge transfer in which an electron is considered to shuttle from one of the collision partners to the other. The computation of the mobility of He$^+$ in He which includes symmetry forces$^{39}$ yields a value (10.2 cm$^2$/V sec) in good agreement with the experimental determined value$^{40}$ (10.8 cm$^2$/V sec). A classical calculation of the mobility which excludes the resonant charge transfer process yields a mobility far too large (18.3 cm$^2$/V sec).$^{41}$

The rate at which the atomic ion undergoes charge-transfer collisions is given by $(\tau_T)^{-1} = \sigma TN$ where $V$ is the relative velocity of the colliding pair and $N$ the ground state density. With a ground state density of $8 \times 10^{16}$ cm$^{-3}$ this gives $\tau_T \sim 5 \times 10^{-7}$ sec. The lifetime of the ion is determined by ambipolar diffusion in the discharge so that

$$
(\tau_0)_{\text{ion}} = \frac{\Lambda^2}{D_a}
$$

(26)

where $D_a$ is the ambipolar diffusion coefficient and $\Lambda$ is the diffusion length. For the atomic ion $D_a = 460$ cm$^2$ mm Hg/sec in the absence of a discharge. In the presence of an electric field

$$
D_a' = D_a \left(1 + \frac{T_e}{T_g}\right)
$$

(27)

where $T_e$ is the electron temperature and $T_g$ is the gas temperature. If we assume $T_e/T_g \sim 100$ they find $(\tau_0)_{\text{ion}} \sim 10^{-5}$ sec. Thus, the most
frequent "event" in the life of the \( \text{He}^+ \) ion is a charge transfer process which results in a transfer of angular momentum to the ions. The atomic ions then acquire the same polarization as the ground state. The loss of angular momentum only occurs via diffusion to the walls where the ions recombine. The loss rate due to this process is just \( n_{\text{ion}}/T_a \) which for reasonable values of the ion density \(< 10^9 \text{ cm}^{-3}\) in the discharge is not sufficiently large to account for the observed loss rate out of the ground state spin system.

The ground state relaxation rate for this process is given by the inverse process

\[
\left( \frac{1}{T_T} \right)^{-1} = \sigma_T V n_{\text{ion}}
\]

where \( V \) is the relative velocity of the colliding particles and \( n_{\text{ion}} \), the ion density. The charge exchange rate is 0.2 sec\(^{-1}\) for an ion density on the order of \( 10^9 \text{ cm}^{-3} \), i.e., every 5 sec (on the average) a ground state atom undergoes a charge exchange collision with an atomic ion. This time is comparable to the spin-exchange time \( T_2 \) for the ground state atom. Consequently if the collision carries away spin angular momentum, the loss rate due to this charge transfer can approach the rate at which the spin-exchange process adds angular momentum to the ground state and seriously degrade the polarization. However, these charge-transfer collisions result only in a polarization of the ion and loss only occurs via ion diffusion to the walls.

**Process (2).** Exciting and ionizing collisions. Ground state atom collisions with electrons having energies less than the first excited state \( 2^3S_1 \), \( E = 19.8 \text{ eV} \) cannot change the state of the atom. Inelastic collisions with electrons having energies greater than 19.8 eV populate
the metastable and higher lying states. These collisions will in
general result in an angular momentum loss out of the ground state.
Since the metastable lifetime is on the order of $2 \times 10^{-3}$ sec a creation
rate of $10^{13}$ sec$^{-1}$ cm$^{-3}$ is required to maintain a metastable density of
$2 \times 10^{10}$ cm$^{-3}$. Thus, losses out of the ground state occur at a rate
$10^{13}$ sec$^{-1}$ cm$^{-3}$. This represents a lower limit to the losses due to
inelastic electron collision with the ground state. A more complete
description would require a knowledge of excited state populations and
lifetimes.

We are able to exclude processes (1) and (2) as significant loss
mechanisms on the basis of experiments in which the discharge was pulsed.
When the discharge is extinguished, the electrons thermalize very rapidly$^{35}$
($< 100$ µsec). The metastable lifetime is, however, much longer (several
milliseconds) so that a condition exists in the afterglow in which the
electron energy is small and the metastable density still high. The loss
rate due to diffusion now proceeds at a much lower rate. Consequently,
angular momentum losses associated with these two processes are consider-
ably reduced, and it should be possible to obtain greater polarizations
by optically pumping in the afterglow of the discharge. In the experi-
ment referred to the discharge was pulsed repetitively. For all cases
observed the resultant polarization was significantly smaller than that
obtained with the steady state discharge. The polarization approached
the maximum value only as the duty cycle of the excitation to the
discharge approached unity. This experiment also tends to confirm our
conclusions concerning the loss mechanisms in the metastable system
(i.e., electron-metastable collisions are not the dominant mechanism
for angular momentum loss of the entire system although they may be for
the metastable system alone).\textsuperscript{16}

Processes (3) and (4). Atom-atom interchange collisions between an atom and a molecule. If a process of the type

\[
\text{He}(\text{I}) + \text{He}_2^*(\text{II,III}) \rightarrow \text{He}(\text{II}) + \text{He}_2^*(\text{I,III})
\]

(28)

occurs where the asterisk designates either a singlet or triplet ($^1\Sigma_g^+$ or $^3\Sigma_g^-$) metastable molecule or the ion molecule and I, II, III represent the nuclear cores which are distinguishable because of their nuclear spin, depolarization can result. This mechanism was first suggested by Watt and Jaspar.\textsuperscript{36} In the triplet metastable atom and the molecular ion, both of which are long-lived species, depolarization can occur as a result of the internal degrees of freedom possessed by the molecule. In the triplet molecule the nuclear spin is coupled to the electronic spin via the hyperfine interaction in the molecule. The resultant spin is then coupled to any orbital and rotational angular momenta present. Each rotational manifold consists of a set of energy levels which differ by the Zeeman energy of the spins in a magnetic field. Collisions are extremely effective in mixing these states among the manifold.\textsuperscript{42} Then, since the nuclear spins are coupled to the electronic spin angular momentum, collisions result in a "memory" loss for the nuclear spin orientation.

In the singlet molecule the electron spins are paired off and the nuclear spins are well shielded. The expectation value for the nuclear spin in this case can only change if the rotational state of the molecule is disturbed. The singlet molecule is, however, unstable and radiation to the ground state molecule can carry off angular momentum.
These processes stand in contrast to the charge-transfer collision in which spin angular momentum is conserved between the colliding particles.

In order to determine the reaction rate for these atom-atom interchange collisions the cross section for the process must be known. In the absence of an accurate theory, an estimate of the magnitude of the cross sections for these processes can be made on the basis of a calculation performed by Guimousis and Stevenson.\textsuperscript{43} Their derivation is based on the classical concept of a reaction cross section and the kinetic theory of gases. Since the interaction potential for the ion-atom pair is of the inverse fourth power, the cross section can be expressed, following Ref. 43 (see also Appendix F), in terms of the polarizability of the He atom:

\[
\sigma_p(v) = 2\pi \left( \frac{\alpha e^2}{M_r v^2} \right)^{1/2}
\]

(29)

where \(\alpha\) is the polarizability, \(e\) the electronic charge, \(M_r\) the reduced mass, and \(v\) the relative velocity of the colliding particles. At 300\(^\circ\)K we find \(\sigma(v) \sim 4 \times 10^{-15}\) cm\(^2\).

The molecular ion density can be obtained by considering the gaseous reactions which result in the formation of the molecular ion. Morris\textsuperscript{44} discusses various reactions:

1. \(\text{He}^+ + 2\text{He} \rightarrow \text{He}_2^+ + \text{He},\)
2. \(\text{He}^+ + \text{He} \rightarrow \text{He}_2^+ + e,\) and
3. \(\text{He}_2^+ + e \rightarrow \text{He}_2^+ + 2e.\)

Pakhomov and Fugal\textsuperscript{45} also suggest the reaction

(4) \(\text{He} + \text{He}^+ + \text{He}^+ \rightarrow \text{He}_2^+ + e + \text{He}.\)
Hackam and Lennon\textsuperscript{46} give the conversion frequency for process (1) above as $115 \, p^2 \, \text{sec}^{-1}$. Thus we can write

$$\frac{[\text{He}_2^+]}{[\text{He}^+]} = \frac{\Lambda^2}{D_a} \, 115 \, p^2$$

(30)

where $[\text{He}_2^+]$ = molecular ion density

$[\text{He}^+]$ = atomic ion density

$\Lambda$ = diffusion length

$D_a$ = ambipolar diffusion coefficient for the molecule.

The diffusion coefficient is given by Eq. (27). This leads to a molecular ion density on the order of $10^7 \, \text{cm}^{-3}$ at a pressure of 2 mm Hg. Boyd and Morris\textsuperscript{47} measured the ratio of molecular ion to atomic ion density and for pressures between 0.1 and 1.0 mm Hg obtained a ratio which increased to 10% at 1.0 mm Hg. If the atomic ion density is taken as $10^9 \, \text{cm}^{-3}$, this would imply a molecular ion density nearer $10^8 \, \text{cm}^{-3}$.

The frequency with which the molecular ion undergoes interchange collisions on the basis of the cross section calculated above is on the order of $6 \times 10^7 \, \text{sec}^{-1}$. Since each ground state ion collision is a depolarizing collision the loss of angular momentum occurs at a rate $3 \times 10^{15} \, \text{sec}^{-1}$ for a molecular ion density of $5 \times 10^7 \, \text{cm}^{-3}$. A loss rate of this magnitude is more than sufficient to account for the observed ground state relaxation. In fact, a cross section for this process which is an order of magnitude smaller than that given by Eq. (29) leads to a loss rate which fits the observations.

The interaction potential for the neutral pair is of the inverse sixth power and arises from the Van der Waal forces between induced dipoles. The magnitude of the cross section for this process can be
derived using a modification of the technique utilized by Guismousis and Stevenson\textsuperscript{43} (see Appendix F). The cross section can be expressed in terms of the Van der Waal's constant and gives

$$\sigma (V) = \frac{3\pi}{2} \left( \frac{4c}{M_p V^2} \right)^{1/3}$$  \hspace{1cm} (31)

where $c$ is the Van der Waal's constant. At 300°C we find $\sigma(V) = 5 \times 10^{-16}$ cm$^2$. The metastable molecule density is obtained from the three body reaction\textsuperscript{39} $\text{He}^M + \text{He} + \text{He} \rightarrow \text{He}_2^0 (\Sigma_g^+) + \text{He}$ which has a conversion rate of 0.2 p$^2$ sec$^{-1}$.\textsuperscript{32} We can then write

$$\frac{[\text{He}_2^0]}{[\text{He}^M]} = \frac{\Lambda^2}{D} 0.2p^2$$  \hspace{1cm} (32)

where

$[\text{He}_2^0]$ = neutral molecule density
$[\text{He}^M]$ = triplet metastable density

$D$ = diffusion coefficient.

At 26 mm pressure and a metastable density of $2 \times 10^{10}$ cm$^{-3}$ we find the molecular metastable density to be $\sim 2 \times 10^8$. This leads to a loss rate due to metastable molecule-ground state interchange collisions which is on the order of $10^{15}$ sec$^{-1}$. Since the ground state relaxation rate obtained earlier was about $6 \times 10^{14}$ sec$^{-1}$, this process would also seem to be able to account for the observed loss rate.

The results of pulsed discharge experiments, however, suggest that the interaction with the molecular ion is the predominant relaxation mode. We recall that pulsing the discharge always results in a lower polarization than the steady discharge. In the afterglow of the discharge
the molecular ion density increases substantially by a conversion of the atomic ion. This has been observed experimentally by Hackam and Lennon, who reported an increase of an order of magnitude in the molecular ion density in the afterglow. This increase is more than adequate to result in a substantially lower polarization (via a higher loss rate) in the afterglow as we have observed.

It should be emphasized that the calculations of the cross sections for interchange were completely classical. It is reasonable to expect that the form of the interaction potential would be very sensitive to the overlap integrals which give rise to resonant exchanges in a quantum mechanical treatment so that further work is required to establish without question the nature of the ground state relaxation.

Until recently the possibility that interactions of the type considered here could occur at all was never suggested. Varney suggested that the reaction \( \text{H}_2(\text{I}) + \text{H}_2^+(\text{II}) \rightarrow \text{H}_2^+(\text{I}) + \text{H}_2(\text{II}) \) for charge exchange occurred as a result of an exchange of the protons rather than a simple exchange of charge (electron). More recently, however, Hasted proposed that reactions of the type

\[
A^+B_x + B_x^+ \rightarrow A^+B_x^+ + B_x
\]

(33)

contribute sufficiently to the diffusion process to account for the anomalous low mobilities of the molecular ions \( \text{H}_2^+ \) in \( \text{H}_2 \), \( \text{N}_3^+ \) in \( \text{N}_2 \) and \( \text{C}_2\text{O}_2^+ \) in Co. He calculates cross sections on the order of \( 10^{-15} \) to \( 10^{-14} \) cm\(^2\) at impact energies of 1 eV. The discrepancy between the experimental and theoretical value of the mobility for \( \text{He}_2^+ \) in He when the polarization model is used could be accounted for by a process of
the type suggested by Hasted.

V. Conclusions

On the basis of the experimental observations we draw the following conclusions.

1. The nuclear polarization produced by the optical pumping process depends strongly on the discharge intensity and increases as the discharge level decreases (see Figs. 9 - 11).

2. A plot of the experimental data for $T_p$ vs $N/n P$ yields a value of $T_p \sim 4 \times 10^{-4}$ sec for our lamps.

3. Experimental observations support the conclusion that $\tau_R / \tau_p > 1$ for sample pressures between 1.0 and 10 mm Hg. At pressures below 1 mm Hg diffusion effects become important while at pressures above 10 mm Hg three body processes become important.

4. At pressures between 1 and 10 mm Hg, $\tau_R$ is determined by electron-metastable collisions involving spin exchange. (The spin exchange can involve triplet-singlet conversion.)

5. Since the polarization is light limited, i. e., proportional directly to $\tau_p^{-1}$, then $\tau_p^{-1} > \tau_R^{-1} or N/n 1/T_R$. Utilizing conclusion (3) we find $1/\tau_R < 1/\tau_p < N/n 1/T_R$ which in turn implies that $T_R \sim T_p$.

6. We then conclude that the dominant loss mechanism limiting the attainment of higher polarizations for a given light intensity is due to interactions of the ground state atom with species created by the electrical discharge.
(7) An examination of various loss processes leads to the tentative conclusion that atom-ion interchange between the ground state atom and the molecular ion and/or metastable molecule is the most likely source of relaxation for the system polarization.

Table V summarizes the observations and conclusions for the particular case for which the metastable density is $1.6 \times 10^{10}$ cm$^{-3}$ and the pressure is 2.6 mm Hg.
## TABLE V: Summary of Results Obtained at 2.6 mm Hg and 2% Absorption

<table>
<thead>
<tr>
<th>Relaxation Time</th>
<th>Measured Value</th>
<th>Suggested Mechanism</th>
<th>Rate of Loss of Angular Momentum</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_p$</td>
<td>$4 \times 10^{-4}$ sec</td>
<td>Absorption of resonance radiation from a He$^+$ lamp</td>
<td>$1.6 \times 10^{13}$ $\text{sec}^{-1}$</td>
</tr>
<tr>
<td>$\tau_R$</td>
<td>$10^{-3}$ sec$^a$</td>
<td>Collisions of He$^M$ atoms with hot electrons (2 ev)</td>
<td></td>
</tr>
<tr>
<td>$\tau_2$</td>
<td>$1.6 \times 10^{-7}$ sec$^b$</td>
<td>Spin exchange with ground state atoms</td>
<td></td>
</tr>
<tr>
<td>$T_2$</td>
<td>9 sec$^b$</td>
<td>Spin exchange of ground state atom with He$^M$</td>
<td></td>
</tr>
<tr>
<td>$T_R$</td>
<td>150 sec</td>
<td>Collisions with discharge products, in particular atom-atom interchange between a ground state atom and the metastable or ion molecule</td>
<td>$5.7 \times 10^{14}$ $\text{sec}^{-1}$</td>
</tr>
</tbody>
</table>

$^a$ After Byerly$^{16}$

$^b$ After Colegrove, et al.$^{26}$
PART II. $^{3}$He NUCLEAR RELAXATION AT LOW PRESSURE

I. Introduction

The first part of this thesis was concerned with relaxation processes associated with interactions of the metastable and ground state atoms with impurities created by the electrical discharge. In this part we are concerned with relaxation of the nuclear spin system in a gas in the absence of the discharge.

The interactions of a magnetic dipole with its surroundings occur via a coupling of the dipole to a fluctuating magnetic field at the resonant frequency of the precessing dipoles. The usual case considered results from collisions with paramagnetic species in which the nuclei experience an appreciable local magnetic field only during a collision or a near collision. Consequently, nuclear dipole-dipole interactions for nuclear spins $I = 1/2$ are generally very long in gases. For $^{3}$He nuclei an estimate of the spin-lattice relaxation time for this interaction at 300$^\circ$K and a gas pressure of 1 mm Hg gives approximately $10^8$ sec. In practice, interactions of the nuclear spins with the container walls or with paramagnetic impurities result in a considerably shorter relaxation time.

The application of optical pumping to the atoms of $^{3}$He as described in Part I results in an impressively large ($\sim 40\%$) polarization of the nuclear spins at gas pressures on the order of several mm Hg and at room temperature. The large polarization at low pressures and long intrinsic spin relaxation time of $^{3}$He nuclei has permitted the observation of a new source of spin-lattice relaxation which occurs when a gas sample is located in an inhomogeneous magnetic field. The effect arises as a consequence of the thermal motion of the spins in the nonuniform
magnetic field. This creates a time varying magnetic field in the frame of reference of the spin. Components at the resonant frequency of the spins lead to the relaxation.

A number of authors have considered the combined effects of translational diffusion and gradients in the applied magnetic field on the relaxation of nuclear spin systems. Such an effect, insofar as it influences the spin-spin relaxation time $T_2$, was analyzed by Hahn\textsuperscript{52} and by Carr and Purcell\textsuperscript{53} in conjunction with their definitive work on nuclear resonance techniques involving free precession. Later, the phenomenological Bloch equations of nuclear magnetic resonance were generalized by Torrey\textsuperscript{54} to include transfer of magnetization by diffusion.

Bloch was the first to point out that translational diffusion in the vicinity of strong irregular magnetic fields could contribute effectively to spin-lattice relaxation, and he proposed using paramagnetic powders as a catalyst for nuclear relaxation in monatomic gases.\textsuperscript{55} This technique was successfully employed by Proctor and Yu to shorten the relaxation time of Xe\textsuperscript{129}, thus allowing measurement of the Xe magnetic moment by nuclear magnetic resonance techniques.\textsuperscript{56}

Kleppner, Goldenberg, and Ramsey in connection with their work on the atomic hydrogen maser derived approximate expressions for $T_2$ and $T_1$, the spin-lattice relaxation time, for the case of spins which are reflected from container walls in the presence of an inhomogeneous magnetic field.\textsuperscript{57}

Quite a different situation from that considered by Kleppner, et al. arises when the mean free path of the diffusing atoms is much smaller than container dimensions, and it is that case, which we shall consider here. In their experiments on optical pumping and nuclear polarization
in low-pressure He$^3$ gas, Colegrove, Scheerer, and Walters observed that even very weak magnetic field gradients completely control the He$^3$ spin-lattice relaxation time. Qualitatively, this decrease in $T_1$ was explained in terms of the fluctuating magnetic field seen by a He$^3$ atom as it undergoes Brownian motion in the presence of the field gradient.

The availability of large nuclear polarizations in a gas has stimulated interest in the development of polarized He$^3$ ion sources and target chambers suitable for use in nuclear scattering experiments. The results reported here are of practical importance in the construction of such apparatus since the relaxation of the He$^3$ nuclei by diffusion through gradients constitutes a "leak" of the angular momentum imparted to the He$^3$ spin system by the circularly polarized pumping light. If the leak is sufficiently large, the polarization will be degraded. The effects of inhomogeneous magnetic fields are particularly apparent in the environment required for optical pumping. The relaxation formula derived in Sec. II provides the necessary guidelines for establishing toleration limits on magnetic field gradients which might result from target or ion source construction materials and from inhomogeneity in the applied magnetic field.

In the sections that follow, a quantitative theory of spin-lattice relaxation caused by the diffusion of spins in inhomogeneous magnetic fields is presented along with a description of experiments which verify in all respects the calculated dependence of $T_1$ on sample pressure, magnetic field strength, and gradient intensity.
II. Theory

Brownian motion in the presence of magnetic field gradients causes the moving atoms to experience randomly fluctuating magnetic fields. Such fluctuating fields contribute to spin-lattice relaxation of the atomic nuclei. Using time-dependent perturbation theory, an expression for the spin-lattice relaxation time, $T_1$, can be derived for a system of spins, $I$, which do not interact with one another but do couple to random external field fluctuations. The applied magnetic field, $H$, is regarded as a superposition of a weak spatially varying field upon a much stronger homogeneous field $H_0$. The Hamiltonian for a spin $I$ in a fluctuating field $h(t)$ and a constant field $H(0, 0, H)$ is

$$
\mathcal{H}(t) = -\gamma H I_z H - \gamma h \mathbf{I} \cdot \mathbf{h}(t)
$$

(34)

where $h(t)$ is the fluctuating field seen by a spin of gyromagnetic ratio $\gamma$ as it executes Brownian motion in the presence of the gradient in the applied magnetic field $H$. If $h(t)$ is small we can apply first-order time-dependent perturbation theory. The starting point is the equation

$$
a_k(t) = -\frac{i}{\hbar} \int_0^t A_{km}(t') e^{i\omega_{km} t'} dt'
$$

(35)

where $|a_k(t)|^2$ is the probability that the system will be in an energy state $E_k$ at time $t$ if it was initially in the state with energy $E_m$. $A_{km}(t)$ is the matrix element of the perturbation Hamiltonian between the two states, and $\omega_{km} = (E_k - E_m)/\hbar$. The transition probability per unit
time \( \hbar \) the level \( k \) is

\[
\omega(t) = \frac{d}{dt} |a_k(t)|^2
\]  

(36)

We wish to consider now the case in which the perturbation Hamiltonian \( -\gamma \hbar \mathbf{I} \cdot \mathbf{\hat{I}}(t) \) represents a random stationary process. From Eq. (2) we see that there will be random fluctuations in \( \omega(t) \) so we define an average transition probability per unit time as

\[
\langle \omega \rangle = \lim_{T \to \infty} \frac{1}{T} \int_{0}^{T} \omega(t) \, dt
\]

\[
= \lim_{T \to \infty} \frac{1}{T} \int_{0}^{T} \frac{d}{dt} |a_k(t)|^2 \, dt
\]

\[
= \lim_{T \to \infty} \frac{1}{T} |a_k(T)|^2
\]  

(37)

From which we find

\[
\langle \omega \rangle = \lim_{T \to \infty} \frac{1}{T} \frac{1}{\hbar^2} \int_{0}^{T} \int_{0}^{T} A_{km}(t') A_{km}^*(t'') e^{i\omega_{km}(t'-t'')} \, dt' \, dt''
\]  

(38)

If we let \( t'' - t' = \tau \) and \( t' = t \) we may show that this reduces to
\[ \langle \omega \rangle = \lim_{T \to \infty} \frac{1}{T} \frac{1}{\hbar^2} \left\{ \int_{-T}^{0} \int_{-\infty}^{\infty} e^{-i\omega \tau} \int_{-\infty}^{T} A_{km}(t) A^*_{km}(t+\tau) \, dt \right\} \]

Taking the limit \( T \to \infty \) we find

\[ \langle \omega \rangle = \frac{1}{\hbar^2} \int_{-\infty}^{\infty} e^{-i\omega_{km} \tau} \langle A_{km}(t) A^*_{km}(t+\tau) \rangle_{\text{AVE}} \, d\tau \]

where

\[ \langle A_{km}(t) A^*_{km}(t+\tau) \rangle_{\text{AVE}} = \lim_{T \to \infty} \frac{1}{T} \int_{0}^{T} A_{km}(t) A^*_{km}(t+\tau) \, dt \]

For a spin 1/2 system it may easily be shown that \( \langle \omega \rangle = 1/2T_1 \). We then arrive at the expression for the spin-lattice relaxation time for a random stationary process

\[ \frac{1}{T_1} = \frac{2}{\hbar^2} \int_{-\infty}^{\infty} e^{-i\omega_{\frac{1}{2}} \tau} \langle A_{\frac{1}{2}-\frac{1}{2}}(t) A^*_{\frac{1}{2}-\frac{1}{2}}(t+\tau) \rangle_{\text{AVE}} \, d\tau \]
where \( \omega_0 \) is the energy difference between the spin states \( |1/2\rangle \) and \( |-1/2\rangle \) in the constant magnetic field \( H_0 \); \( \omega_0 = \gamma H_0 \).

The matrix elements \( A_{1/2 - 1/2}(t) \) for our problem can be evaluated for the perturbation Hamiltonian in Eq. (34). Thus

\[
A_{1/2 - 1/2}(t) = -\gamma \hbar \sum_{j=x,y,z} h_j(t) \langle \frac{1}{2} | I_j | -\frac{1}{2} \rangle
\]

(43)

where \( h_j(t) \) is the \( j^{th} \) component of the field fluctuation. Substituting the results of Eq. (42) into Eq. (41) we get

\[
\frac{1}{T_1} = \frac{\gamma^2}{2} \int_{-\infty}^{\infty} e^{-i\omega \tau} \left\{ \langle h_x(t)h_x(t+\tau) \rangle_{\text{AVE}} + \langle h_y(t)h_y(t+\tau) \rangle_{\text{AVE}} \right\} d\tau
\]

(43)

if we assume that \( h_x(t) \) and \( h_y(t) \) are statistically independent.

Thus the problem reduces to one of finding an expression for the quantities \( g_j(\tau) = \langle h_j(t)h_j(t + \tau) \rangle_{\text{AVE}} \) and

\[
G_j(\omega) = \int_{-\infty}^{\infty} e^{-i\omega \tau} g_j(\tau) d\tau
\]

which are defined as the autocorrelation and spectral density functions for the process \( h_j(t) \) respectively.

In the case considered here, the field fluctuations occur as a result of the Brownian motion of the spins in the presence of a magnetic field gradient. For simplicity we consider a field gradient which is constant and axially symmetric with respect to the sample and with the variation
of H over the sample being small compared to \( H_0 \).\(^{63}\)

As discussed later, our experimental conditions easily met these requirements. Under such circumstances, the autocorrelation functions \( g_x(t) \) and \( g_s(t) \) are equal. The spectral density functions may be evaluated in either of the two equivalent ways described below.

**A. Rotating Reference Frame Derivation**

Considerable physical insight into gradient relaxation mechanisms can be gained by considering a spin which is initially at an arbitrary point within the sample and choosing the z axis at that point to lie along the local magnetic field direction. Let the y axis be chosen so that the velocity vector of the atom lies in the y-z plane. As the spin moves away from its initial position with a velocity whose y component is \( U_y \), it sees the field direction rotating about the x axis with an angular velocity

\[
\omega_R = \frac{1}{H} \left( \frac{\partial H_y}{\partial y} \right) U_y
\]

We wish to view the problem in a reference frame in which the z axis always coincides with the local magnetic field direction as seen at any instant by the moving spin; that reference frame is simply one which rotates about the x axis with angular velocity \( \omega_R \). In this frame, as discussed, for example by Slichter,\(^{64}\) the spin sees an additional field in the direction of rotation. This additional field is

\[
H_{\text{eff}} = \frac{\omega_R}{\gamma} = \frac{1}{\gamma H} \left( \frac{\partial H_y}{\partial y} \right) U_y
\]

\((45)\)
Fig. 19 As the spin moves from position $p$ to $p'$ with a velocity $U_y$, the $y$ component of field increases from zero to $H_y$. This gives rise to a rotation of the resultant field through the angle $\theta$. Transformation to a frame rotating with $H$ gives rise to an effective field along the $x$ axis as discussed in the text.
and appears in the x direction. The physical picture is illustrated in Fig. 19. The nuclear moment precesses about the resultant field \( \mathbf{H} + H_{\text{eff}} \) and begins to depart from its original orientation along the laboratory z axis. The precession about the effective field continues as long as these conditions remain.

Now consider the effect of an atomic collision which alters the particle velocity. The spin starts moving in a new direction, and to keep the z axis coincident with the local magnetic field direction we must abandon our original rotating reference frame and transform to a new frame which rotates about an axis in the transverse plane which is perpendicular to the new transverse velocity. \( H_{\text{eff}} \) then points in a new direction in the x-y plane. Subsequent collisions require similar coordinate transformations. Thus, in a reference frame where the z axis is always along the local magnetic field direction, atomic motion through gradients in \( H \) causes a magnetic field \( H_{\text{eff}} \) to appear in the x-y plane, and collisions cause \( H_{\text{eff}} \) to fluctuate in both direction and magnitude. This fluctuating transverse effective field can induce magnetic dipole transitions, and it is the autocorrelation function for \( H_{\text{eff}}(t) \) that we require in Eq. (43) for the relaxation time \( T_1 \). The autocorrelation function for this process can be written as

\[
\langle h_x(t) h_x(t+\tau) \rangle_{\text{ave}} = \left[ \frac{1}{\gamma H} \left( \frac{\partial H_y}{\partial y} \right) \right]^2 \langle U_y(t) U_y(t+\tau) \rangle_{\text{ave}}
\]

(46)

Since we are concerned with stationary perturbations (as a result of the Brownian motion of the spins), the time average of \( U_y(t) U_y(t+\tau) \) is equivalent to the ensemble average.
The modern theory of Brownian motion of a free particle of mass $m$ generally starts with the ensemble equation of motion

$$\frac{d\vec{U}}{dt} + \beta \vec{U} = \vec{R}(t)$$

(47)

where $\vec{R}(t)$ is a random force acting on the particles and $\beta$ is a constant representing a dynamical "friction" which opposes the motion of the particle in the medium. $\vec{U}(t)$ is then the stochastic variable representing an ensemble of particle velocities. The autocorrelation function for $U_i(t)$ is given by

$$\langle U_i(t+\tau)U_i(t) \rangle_{\text{AVE}} = \langle U_i^2 \rangle e^{-\beta \tau}$$

(48)

where $\beta^{-1}$ is the correlation time and is approximately the mean time between atomic collisions, $\tau_c$ and $\langle U_i^2 \rangle$ is the mean squared $i$ component of velocity. Substitution of Eqs. (46) and (48) into the $T_1$ expression and evaluation of the integral yields

$$\frac{1}{T_1} = \frac{2}{3} \frac{\langle \partial H_y \rangle^2}{H_s^2} \langle \xi^2 \rangle = \frac{\tau_c}{1 + \omega_0^2 \tau_c^2}$$

(49)

where we have used for the mean-squared velocity

$$\langle \xi^2 \rangle = 3 \langle \xi_x^2 \rangle = 3 \langle \xi_y^2 \rangle$$

and, by symmetry,

$$\left( \frac{\partial H_y}{\partial y} \right) = \left( \frac{\partial H_x}{\partial x} \right)$$
B. Laboratory Reference Frame Derivation

Alternatively, the $T_1$ expression may be derived using the laboratory reference system. Since there is no unique axis of spin quantization, let us choose an origin of coordinates at an arbitrary point in the sample with the $z$ axis parallel to $H_0$. Because of the gradient in $H$ a spin moving about in the sample container sees variable $x$- and $y$-components of field relative to the fixed coordinate axes just defined. In terms of its position coordinates, the magnetic field seen by a spin is

$$H = -i \frac{\partial}{\partial x} G_x - i \frac{\partial}{\partial y} G_y + \kappa (2Gz + H_0)$$

(50)

where $G = \frac{\partial H_F}{\partial x} = \frac{\partial H_F}{\partial y}$ gives the magnitude of the constant field gradient. Thus

$$h_x(t) = -G x(t) \quad h_y(t) = -G y(t)$$

and

$$\langle h_x(t) h_x(t+\tau) \rangle_{\text{ave}} = G^2 \langle x(t) x(t+\tau) \rangle_{\text{ave}}$$

(51)

Now, if we consider the displacement of a particle in Brownian motion, we find that the random process represented by $x(t)$ is not stationary since $\langle x(t)^2 \rangle$ increases without limit as $\tau$ increases and its autocorrelation function does not exist. However, the process does possess stationary increments, i.e., $\langle x(t + t_o) - x(t_o) \rangle$ is stationary. In this situation we can represent a nonstationary process with stationary increments as a limit of a sequence of stationary processes.

[Physically, we do not care about the position $x(t)$ of the spin; rather,
we are concerned with the fluctuations in \( x(t) \), which are related to the incremental motion. Thus, consider the ensemble equation of motion for the displacement of a Brownian oscillator:

\[
\frac{d^2 x}{dt^2} + \beta \frac{dx}{dt} + \lambda^2 x = h(t)
\]  

(52)

The autocorrelation function for \( x(t) \) is well known and its Fourier transform is easily evaluated. Upon taking the Fourier transform, one lets the force constant go to zero and the result is the desired spectral density function for a free particle,

\[
\int_{-\infty}^{\infty} \langle x(t)x(t+\tau) \rangle e^{-i\omega \tau} \, d\tau = 2 \langle U_x^2 \rangle \frac{\tau_c}{\omega^2 (1 + \omega^2 \tau_c^2)}
\]  

(53)

where \( \langle U_x^2 \rangle \) is the mean-squared \( x \)-component of particle velocity, and \( \tau_c \) is the mean time between atomic collisions. Using \( \langle U_x^2 \rangle = 1/3 \langle U^2 \rangle \) and substituting into Eq. (43), we obtain

\[
\frac{1}{\tau_i} = \frac{2}{3} \kappa \xi G \langle U^2 \rangle \frac{\tau_c}{\omega^2 (\omega^2 \tau_c^2 + 1)}
\]

which is identical to the result obtained in Sec. IIA.
III. Experimental Techniques

The theory developed in Sec. II was verified experimentally by spin-lattice relaxation time studies of gaseous He³ samples subjected to known magnetic field gradients. To test the predicted dependence of T₁ on Tc and H₀, measurements were made over a range of He³ gas pressures from 0.2 mm to 10 mm Hg, and for magnetic field strengths ranging from 1 gauss to 240 gauss. The He³ samples were contained in 60 cc Pyrex spheres.

Relaxation times were measured by monitoring the decay of He³ spin magnetization from an initially highly polarized state. Optical pumping methods described in Part I were used to produce the spin polarization. For the experiments reported here, He³ polarizations between 5% and 10% were typical.

To measure T₁, the sample was first polarized by the optical pumping technique. Then the electrical discharge was turned off, thus providing the desired highly polarized state of the unexcited He³ gas. The sample magnetization then decays with time constant T₁ to its thermal equilibrium value. In the absence of magnetic field gradients the decay times were always greater than one hour, spin relaxation in that case resulting from interactions of the He³ nuclei with the container walls. The gradient-dominated relaxation times were always much smaller, so that wall relaxation effects could be safely neglected.

The magnetization measurements were made in a 220 gauss magnetic field and in the following sequence. Immediately after turning off the electrical discharge, the nuclear magnetic resonance signal is observed by conventional slow passage NMR techniques at 714 kcps. The strength of the NMR signal is proportional to the initial magnetization, M₀. The
applied magnetic field is then changed to the value $H_0$ at which the gradient-dominated relaxation time is to be measured, and the known gradient is applied for a time $\Delta t$. After the gradient is turned off, the field is returned to 220 gauss, and the residual magnetization $M$ is measured. The relative strengths of the initial and residual NMR signals, along with $\Delta t$, allow calculation of $T_1$, assuming an exponential decay. The entire sequence was always completed in a time much less than the relaxation time of the He$^3$ in the absence of gradients.

An alternative optical method for measuring $T_1$ was also used. The measurement sequence was the same as that previously described with the exception that the sample polarization was determined optically instead of by NMR. Optical determination of the polarization is possible because the percentage of the $2^3S_1 - 2^3P_0$ pumping light that is absorbed by the sample depends on the degree of polarization of the sample. The physical basis for this dependence and the experimental techniques for measuring the polarization optically has been fully discussed in Part I.

The optical method has the disadvantage that the electrical discharge must be turned on to populate the $2^3S_1$ state prior to making the absorption measurement. For the residual polarization determination after application of the magnetic gradient, the discharge must be re-ignited and the measurement made in a time short enough so that there is no appreciable change in the polarization due to re-pumping by the measuring light. Typically, the optical pumping time exceeds 30 seconds except at the lowest pressures and the polarization measurement can be made in about one second. An advantage of the optical technique over the NMR method is the greater accuracy obtainable because of better signal-to-noise ratio. The optical technique was used exclusively for the
relaxation measurements at the low fields (~ several gauss).

The external magnetic field was provided by a solenoid end corrected to sixth order. It was patterned after coils studied by Garrett.\(^6\)\(^7\)
The solenoid was wound on a 10 in. diam double-walled aluminum form with ten layers of No. 22 heavy Nylad wire. The field variation over the 5 cm diam sample cell at 220 gauss was about 5 milligauss. Measurements of this homogeneity were made by observing the line width of a pure water sample occupying the same volume as the sample. The field as a function of positions within the solenoid was obtained by measuring the frequency at which the He\(^3\) optical resonance occurred. The motional narrowing of the resonance provides a convenient averaging of the field over the sample. The field variation is shown in Fig. 20. The solenoid was powered by a Varian power supply current controlled to one part in \(10^5\).

The NMR experiments were performed using an Anderson bridge\(^2\)\(^8\) tuned to 714 kc. The rf coil was wound on a 5.3 cm diam polyethelene form and consisted of two 21-turn windings. Each winding was 0.6 cm long and were spaced 4.7 cm apart in order to provide an entrance and exit port for the light beam. The coil inductance was about 100 \(\mu\)h. Signals from the bridge were detected and amplified by a National HRO-60 radio receiver and the output recorded on a Moseley x-y recorder. The 714 kc input to the bridge was provided by a Hewlett-Packard signal generator. Signals could be observed in dispersion and absorption. All measurements were made in an intermediate passage condition, i.e., the conditions for neither slow passage nor adiabatic fast passage were satisfied. This point is discussed more fully in Appendix D.
The field gradient was provided by a large (40 cm diam) set of Helmholtz coils connected in opposition. This provided an easily calculable uniform gradient over the sample at the coil center. The gradient was also measured by observing the increase in the line width of a $^4$He resonance signal when the "Holtzhelm" coils were energized.

At low fields (~ several gauss) a series of experiments were conducted utilizing a small bar magnet. In the far field region of the dipole the gradient is approximately constant over the sample.
Fig. 20  
Solenoid Field Variation

H ~ 230 Gauss

10 milligauss
5 cm

center
IV. Results

$\text{He}^3$ relaxation times for gradients up to 1 gauss/cm were measured over a range of pressures from 0.2 mm Hg to 10 mm Hg and in fields from 1 gauss to 240 gauss. These ranges are sufficiently broad to test the theory over the entire range from $\omega_0\tau_c \ll 1$ to $\omega_0\tau_o \gg 1$.

The effects of walls on the relaxation times were obtained in the absence of gradients ($\sim 1$ milligauss/cm). The results are summarized in Table VI. The relaxation times in the presence of the gradients used in this experiment were always considerably shorter than the shortest relaxation time indicated in the table.

At low magnetic fields for which $\omega_0\tau_c \ll 1$ the expression for the relaxation time reduces to

$$\frac{1}{T_1} \sim \frac{2}{3} G^2 \langle u^2 \rangle \frac{\tau_c}{H_0^2}$$

Thus, $T_1$ is directly proportional to $H_0^2$ and pressure and inversely proportional to the square of the gradient. The results of experiments conducted in this region confirm these predictions. Figures 21-23 summarize these results.

The experimental results over a considerably wider range of $H_0$ and $G$ were also obtained and the results shown in Figs. 24 and 25. The solid lines are derived from Eq. (49). In calculating the theoretical curves, measured values of $H_0$ were used and the gradient was calculated from the coil geometry and current. The mean-squared velocity was taken as $\langle u^2 \rangle = 3kT/m$. All measurements were made at 300°K. The only remaining variable on the right hand side of Eq. (49) is $\tau_c$, the mean time between collisions, which varies inversely with the pressure. Pressures were
<table>
<thead>
<tr>
<th>Sample</th>
<th>Pressure</th>
<th>Relaxation Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Bare Pyrex</td>
<td>1 mm</td>
<td>1.1 - 1.6 hr</td>
</tr>
<tr>
<td></td>
<td>3 mm</td>
<td>1.6 hr</td>
</tr>
<tr>
<td></td>
<td>0.4 mm</td>
<td>1.7 hr</td>
</tr>
<tr>
<td>2. Pyrex + Rb(^a)</td>
<td>1 mm</td>
<td>4 - 7 hr</td>
</tr>
<tr>
<td>3. Pyrex + Dichlorosilane</td>
<td>1 mm</td>
<td>1.1 hr</td>
</tr>
<tr>
<td>4. Pyrex + Rb + Dichlorosilane(^b)</td>
<td>1 mm</td>
<td>4 hr</td>
</tr>
</tbody>
</table>

\(^a\) The variation in relaxation times is probably due to the completeness of the Rb metal coverage of the pyrex. The longest relaxation time was obtained after the Rb metal was carefully distributed over the entire glass surface and the excess metal driven into the tip-off tube.

\(^b\) Trade-name GE Dri-Film
Fig. 21  Relaxation time vs $H_0^2$ for a fixed gradient.

Fig. 22  Relaxation time vs the inverse of the square of the field gradient.

Fig. 23  Relaxation time vs pressure, $H_0$ and gradient constant.
Fig. 24 Relaxation by gradients as a function of applied field at various pressures. The solid lines in each case are calculated from Eq. (49). The vertical scale is plotted in units of $T_1 G^2$ where $G$ is the gradient $\partial H / \partial x$. The gradient was chosen to be either 1.6 or 0.8 G cm$^{-1}$ to keep $T_1$ within convenient limits. The value of $T_C$ is obtained from the minima of the curves shown in Fig. 25. The value of $T_C$ can also be obtained by considering the cross overs of the various curves.
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Fig. 25 Relaxation by gradients as a function of pressure. The solid curves are calculated from Eq. (49). A best fit to the experimental points shown gives $\tau_c = 2.2 \times 10^{-7}$ sec at 1 mm Hg assuming $T_1$ is a minimum at $\omega_0 \tau_c = 1$. 

$T_1 G^2$ (sec.gauss$^2$.cm$^{-2}$) 

Pressure in mm Hg

- $H = 220$ gauss
- $H = 169$ gauss
- calculated
measured at the time of sample preparation using a high-pressure thermocouple gauge previously calibrated against a precision McLeod gauge. The relation between $\tau_c$ and reciprocal pressure could be calculated from the known helium-helium elastic collision cross section derived from gas-kinetic interpretation of viscosity and diffusion data; however, we instead determined the proportionality constant from the data of Fig. 25 by requiring that the minimum in the theoretical curve of $T_1$ versus pressure at $\omega_o \tau_c = 1$ coincide with the $T_1$ minimum found experimentally. This procedure gives $\tau_c = (2.2 \pm 0.2) \times 10^{-7} \ p^{-1}$ seconds at $300^\circ K$, where $p$ is in mm Hg. The elastic collision cross section is then found from $\sigma = (\tau_c v n)^{-1}$ where $v$ is the rms atomic velocity and $n$ the density of the $H_3^+$ in atoms/cc. In view of the excellent agreement between theory and experiment, it is reasonable to regard this work as providing a new independent determination of $\tau_c$. It is in good agreement with the values calculated from viscosity and diffusion data.

An interesting feature of this relaxation mechanism is the change in $T_1$ dependence from $T_1 \sim pH_0^2$ when $\gamma_H \tau_c \ll 1$ to $T_1 \sim p^{-1}H_0^4$ for $\gamma_H \tau_c \gg 1$. This accounts for the cross overs that occur between curves representing different pressures in Fig. 24. The cross over points are also useful in obtaining $\tau_c$ since from Eq. (49) we find

$$\left(\frac{P_1}{P_2}\right) = \omega^2 \tau_{c2}^2$$

where $P_1$ and $P_2$ are the pressures at the cross over, $\omega$ is the resonant frequency at this point, and $\tau_{c2}$ is the collision time at pressure $P_2$.

As an example of a typical experimental measurement, a gradient of 1.5 gauss/cm$^{-1}$ gave a relaxation time of 20 seconds for $He^3$ gas at 0.4 mm pressure in an $H_0$ field of 240 gauss. At 110 gauss, a gradient of
0.43 gauss cm$^{-1}$ produces the same $T_1$. In the absence of a gradient the relaxation time was in excess of 3600 seconds.

This relaxation mechanism becomes extremely important in low pressure gases in weak magnetic fields where even the gradients due to nearby test equipment may be sufficient to drastically affect $T_1$. 
V. Conclusions

The fluctuating magnetic field seen by a spin executing Brownian motion in the presence of a magnetic field gradient contributes to spin-lattice relaxation. The theory developed in Sec. II provides a quantitative relationship between $T_1$, gas pressure, magnetic field strength, gradient strength, and thermal velocity. The experimental results reported in Sec. III verify the theory in every respect over a wide range of all variables.

Under normal circumstances involving NMR studies of high pressure gases and liquids using normal laboratory magnetic fields, gradient relaxation is usually negligible. However, for gases at low pressures and in weak magnetic fields, gradient relaxation is dominant unless one exercises extreme care in providing a highly homogeneous magnetic field over the sample and keeps all ferromagnetic materials out of the general vicinity of the sample. Experiments involving optical pumping of He$^3$ gas are generally done under such low pressure and weak field conditions, and the He$^3$ nuclear polarization attainable by optical pumping is seriously degraded if gradients aren't assiduously avoided.

In particular, one must avoid even slightly ferromagnetic materials in the construction of He$^3$ optical pumping samples. This is especially troublesome in the development of polarized He$^3$ ion sources, and in the design of polarized He$^3$ target cells suitable for use in nuclear scattering experiments where one is often faced with the need for thin metallic foils, electrical feedthroughs, gas valving, and particle counters within the target chamber.

Similar care must be exercised in operation of the optically pumped He$^3$ maser, first reported by Robinson and Myint, and the He$^3$ nuclear magnetometer reported by Schearer, et al.
The long relaxation times observed when the gradients are minimal suggests some interesting properties associated with the nature of the Pyrex surface. The one hour relaxation times observed at 1 mm Hg and room temperature can only be explained if one assumes that the collision time for the He$^3$ atom is considerably longer than usual collision times ($10^{-13}$ sec). It has been suggested$^{70}$ that a monolayer of He is adsorbed on the glass surface and that in a collision a polarized atom exchanges positions with an adsorbed atom. The "sticking" time in this case can be quite long. However, the adsorption energy of He on Pyrex is about .015 eV so that the formation of a monolayer is unlikely. A more reasonable explanation can be found in the results of Cornaz.$^{71}$ Based on experimental observations of relaxation at higher pressures and smaller samples, he concludes that the Pyrex walls are extremely porous and that once a He$^3$ atom enters the rather open glass lattice it leaves only with difficulty. Relaxation while in close proximity with the glass occurs via interaction with paramagnetic impurities.

The sample cell in which Rb is present exhibits a considerably longer relaxation time ($\sim 7$ hr). It is possible that the Rb metal deposited on glass surface in effect "clogs" the open lattice and inhibits the diffusion of He into the Pyrex.

The long nuclear relaxation time of He$^3$ also provides a method for setting a new upper limit on the size of the electric dipole moment of the He$^3$ nucleus. Parity conservation (P invariance) and the invariance of the Hamiltonian to time reversal (T invariance) preclude the existence of permanent electric dipole moments in fermions. However, the recent observation of the decay process $K^0_2 \rightarrow 2\pi$ $^{72}$ suggests that a CP noninvariant interaction probably exists and is a primary source of
noninvariance in the electromagnetic properties of the weak interaction. The presence of an intrinsic electric dipole moment could cause electromagnetic interactions of nucleons to be separately T and P noninvariant. Salzman and Salzman are able to calculate the magnitude of the electric dipole moment for several fundamental particles assuming that a CP noninvariant interaction explains the $K_2^0 \rightarrow 2\pi$ observations. Their results are shown below along with experimentally obtained upper bounds to the magnitudes.

<table>
<thead>
<tr>
<th>Particle</th>
<th>Theoretical Value</th>
<th>Experimental Upper Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron</td>
<td>$\sim 5 \times 10^{-24}$ e cm</td>
<td>$2 \times 10^{-21}$ e cm</td>
</tr>
<tr>
<td>Muon</td>
<td>$\sim 1 \times 10^{-21}$ e cm</td>
<td>$2 \times 10^{-16}$ e cm</td>
</tr>
<tr>
<td>Neutron</td>
<td>$\sim 1 \times 10^{-20}$</td>
<td>$2.4 \times 10^{-20}$ e cm</td>
</tr>
<tr>
<td>Proton</td>
<td>$\sim -1 \times 10^{-20}$</td>
<td>$1.3 \times 10^{-13}$ e cm</td>
</tr>
</tbody>
</table>

Purcell has shown that if a nucleus possesses an electric dipole moment that relaxation can occur via the interaction of the electric dipole $\mu_e$ with the fluctuating electric field at the nucleus during collisions. The relaxation time in this case is given by

$$\frac{1}{T_i} = \frac{8\mu_e^2 mkT \omega_0^2 \tau_e}{h^2 Z^2 e^2 (1 + \omega_0^2 \tau_e^2)}$$

In the absence of magnetic field gradients the relaxation time of the He$^3$ nuclear spins in a carefully prepared sample at 1 mm Hg and 240 gauss ($\omega_0 \tau_c = 1$) is greater than 6.7 hr. Using Eq. (55) we can set a new upper limit on the size of the electric dipole moment of the He$^3$ nucleus.
\( \mu_e < 7 \times 10^{-15} \text{ cm.} \) With care it should be possible to reduce this limit at least another order of magnitude.
REFERENCES


24. F. D. Colegrove, private communication.


29. A physical description of the end corrected solenoid and Helmholtz coils are described in Part II, Sec. III.


34. In this and succeeding sections where gaseous reaction involving the discharge products are discussed we wish to emphasize the following two points: (a) No experiments were conducted which directly determine metastable, ion, or electron densities, and electron temperature or ion mobilities, or cross section for various reactions. These experiments are frequently sophisticated and
always difficult to properly interpret; and (b) The literature by
no means provides a unanimous description of the various reactions
and papers by different authors respected in their fields on the
same subject are frequently at variance.

38. E. W. McDaniel, Collision Phenomena in Ionized Gases (John Wiley
(1957).
51. N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. 72, 679
(1948).
58. Equation (11) for $T_1$ in Ref. 18 is incorrect and should be replaced by Eq. (50) of this thesis.
62. If the $E_k$ and $E_m$ are not well defined states a distribution function $\rho(\omega)$ can be introduced where $\rho(\omega) d\omega = g(E) dE$ is the probability that a state having an energy between $E$ and $E + dE$ is occupied. The treatment of A. Yariv and W. H. Louisell, Phys. Rev. 125, 558 (1962) can then be followed.
63. This statement is unnecessarily restrictive since the statistical nature of the process is established after a few collisions. It can be shown that the appropriate restriction is actually to limit to small values the variation in the magnetic field over the distance the atom diffuses in several mean free paths.
64. C. P. Slichter, Principles of Magnetic Resonance (Harper and Row, New York, 1963), Chap. 2.


76. This calculation was first carried out by M. De Wit, Texas Instruments Incorporated, Dallas, Texas.


APPENDIX A: RELATIONSHIP BETWEEN
OBSERVABLES AND LEVEL POPULATIONS

The observable in all optical pumping experiments is the intensity of a light beam which passes through an absorption cell containing the species to be optically oriented. In this appendix we wish to express explicitly the relationship between the resonance radiation transmitted through the sample cell and the properties of the absorbing atoms.

If $F$ is the total light incident on the absorbing atoms and $S$ is the flux removed from the light beam by absorption, then the transmitted light $T$ is given by the quantity $T = F - S$. The quantity $S$ can be expressed as

$$S = \sum_{F, M_F} \int_{\nu}^{\nu} L_q(\nu) P_{\nu}^3(J, F, M_f) \, d\nu$$

$$P_{\nu}^3(J, F, M_f) = \sum_{J', F', M_f'} P_{\nu}^3(J, F, M_f; J', F', M_f')$$

where $P_{\nu}^q(J, F, M_f; J', F', M_f')$ is the probability per unit time that the incident radiation at frequency $\nu$ and polarization $q$ will induce a transition from the initial state $|J, F, M_f\rangle$ to the excited state $|J', F', M_f'\rangle$. $L_q(\nu) \, d\nu$ is the light intensity of polarization $q$ with frequencies between $\nu$ and $\nu + d\nu$. $p_{F M_f}$ is the probability that the state of total angular momentum $F$ and whose z-component of angular moment is $M_f$, is occupied. The sums are to be taken over each of the
F manifolds for each value of J. If the light intensity is constant over the absorption line, \( P_\nu (J, F, M_f; J', F', M_f') \) does not vary with frequency, and \( S \) becomes for right-hand circularly polarized light

\[
S = \sum_{F, M_f} \sum_{J', F'} P(J, F, M_f; J', F', M_f') \int_0^\infty L(\nu) d\nu
\]

The transition probabilities for electric dipole transitions are determined from

\[
P(J, F, M_f; J', F', M_f') = |\langle J, F, M_f | \bar{R} | J', F', M_f' \rangle|^2
\]

where \( \bar{R} \) is the electric dipole moment operator. The selection rules for \( J \) and \( F \) require that \( J' = J, J \pm 1 \) and \( F' = F, F \pm 1 \).

The light intensity \( L(\nu) \) is also a function of the penetration depth \( x \) of the light into the absorption cell. Thus \( dL(\nu, x) = -k L(\nu, x) dx \). The constant \( k \) in general varies with the frequency of the absorption line. For simplicity we can represent \( k(\nu) \) by a constant \( k_j \) for each of the discrete absorption lines. We then have \( L_j(x) = L_j(0) e^{-k_j x} \) for the \( j \)th absorption line. Frequently, it is sufficient to replace \( L_j(x) \) by some average intensity \( \bar{L}_j \).

The matrix elements for the case of He\(^3\) optical pumping and in which the source of resonance radiation induces transitions to the \( 2^3P_o \) level only become

\[13\]
(a) \[ \langle F J | R \mid F' J' \rangle \frac{1}{2} \sqrt{ (F - M_{\phi})(F + M_{\phi} + 1) (J + i J') } \] for \( F = F' \)

(b) \[ \pm \langle F J | R \mid F' - 1, J' \rangle \frac{1}{2} \sqrt{ (F - M_{\phi})(F - M_{\phi} + 1) (J + i J') } \] for \( F - 1 = F' \)

Removing the \( J \) dependence on the matrix elements we find:

(a) \[ \langle J | R \mid J - 1 \rangle \frac{\sqrt{P(F) P(F - 1)}}{2 F \sqrt{ (2 F - 1)(2 F + 1) } } \] for \( J' = J - 1 \)

(b) \[ \langle J | R \mid J \rangle \frac{\sqrt{P(F) Q(F)}}{2 F (2 F + 1) } \] for \( J' = J - 1 \)

where \( P(F) = (F - I + J)(F + I + J + i) \) and \( Q(F) = (J + I - F)(F + I - J + 1) \).

We then arrive at the results for the transition probabilities for the transitions shown.

\( F = \frac{3}{2}, M_{\phi} = -\frac{3}{2} \rightarrow F = \frac{1}{2}, M_{\phi} = -\frac{1}{2} \sim \frac{A^2}{2} \)

\( F = \frac{3}{2}, M_{\phi} = -\frac{1}{2} \rightarrow F = \frac{1}{2}, M_{\phi} = \frac{1}{2} \sim \frac{A^2}{6} \)

\( F = \frac{1}{2}, M_{\phi} = -\frac{1}{2} \rightarrow F = \frac{1}{2}, M_{\phi} = \frac{1}{2} \sim \frac{A^2}{3} \)

For \( J = 1 \) and \( I = \frac{1}{2} \)
The optical signal can then be expressed as

\[ S_{\text{opt}} = L_1 \sum_{M_f} P_{M_f}^{F, \frac{1}{2}, \frac{3}{2}} \left( \frac{3}{4} - 2M_f + M_f^2 \right) + L_2 \sum_{M_f} P_{M_f}^{F, \frac{3}{2}, \frac{3}{2}} \left( \frac{3}{4} - M_f - M_f^2 \right) \]

The matrix elements for the other transitions are obtained in a similar manner. The results are shown in Table III.
APPENDIX B: SPIN EXCHANGE AND SCATTERING COEFFICIENTS

I. Introduction

The collision between a triplet metastable He\(^3\) atom and a ground state He\(^3\) atom in which angular momentum is transferred between the colliding particles is an important source of relaxation. The quantities \(T_2\) and \(\tau_2\) have been used to characterize the relaxation times of the ground state and triplet metastable state atoms due to these exchange collisions. These relaxation times can be expressed in terms of a cross section for exchange, the relative velocity of the colliding particles, and the density.

Theoretical calculations of the magnitude of the exchange cross section, which is in effect the resonant transfer of energy between the colliding pair, have been carried out by Buckingham and Dalgarno\(^77\) and Brigman, Brient, and Matson.\(^78\) Experimental investigations of the cross section have been conducted by Colegrove, Schearer, and Walters.\(^26\) It is our purpose in this appendix to calculate the relative amplitudes for scattering into the various states \(|F, I, J, M_F\rangle\) given the initial states of the colliding pair.

If the colliding atoms have unpaired spins, then the feature which gives rise to the transfer of angular momentum is the identity of the electrons and nuclei. When two He atoms collide \((1S_o, 2S_1)\) they form a molecule in one of the \(3\Sigma_g^+\) or \(3\Sigma_u^-\) states depending upon whether the spin angular momenta combine in a symmetric or antisymmetric state. These states, having a very different interaction potential, will evolve at different rates during a collision.
II. Wave Functions of the System \( H_e^M \) - He

The unperturbed wave functions for the ground state and triplet metastable state are constructed from atomic wave functions following the method of Heitler and London. We assume there is no spin-orbit coupling so that the wave functions can be separated into products of nuclear spin and electron spin wave functions.

The ground state wave function is given by

\[
\Phi | A_{1,2} (JIFM_f) \rangle \rightarrow \begin{cases} \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & -\frac{1}{2} \end{cases} \begin{align*} a_{11}(1,2) \tilde{\chi}_0 (1,2) a(A) \\ a_{11}(1,2) \tilde{\chi}_0 (1,2) b(A) \end{align*}
\]

where \( A \) labels the nuclear core, \( a \) and \( b \) are the nuclear spin coordinates, \( a_{11}(1,2) \) is the radial wave function for electron 1 and 2 in a 1S orbital, and \( \tilde{\chi}_0 (1,2) \) is the electronic spin wave function.

The triplet metastable wave functions are

\[
F = \frac{3}{2} \\
\Phi | B_{3,4} (JIFM_f) \rangle \rightarrow \begin{cases} \frac{3}{2} \\ \frac{1}{2} \end{cases} \begin{align*} b_{12} (3,4) \left[ \chi_1 (3,4) \ a(B) \right] \\ b_{12} (3,4) \left[ \sqrt{\frac{2}{3}} \chi_0 (3,4) \ a(B) + \sqrt{\frac{1}{3}} \chi_{-1} (3,4) b(B) \right] \\ b_{12} (3,4) \left[ \chi_{-1} (3,4) \ b(B) \right] \\ b_{12} (3,4) \left[ \sqrt{\frac{2}{3}} \chi_0 (3,4) \ b(B) + \sqrt{\frac{1}{3}} \chi_1 (3,4) a(B) \right] \end{align*}
\]
where \( b_{12}(3, 4) \) is the radial wave function for electron 3 in a 1S and electron 4 in a 2S orbital. \( \chi_i (3, 4) \) are the electron spin functions.

The electron spin functions are given by

\[
\begin{align*}
\tilde{\chi}_o (1, 2) &= \frac{i}{\sqrt{2}} \left[ \alpha(1) \beta(2) - \alpha(2) \beta(1) \right] \\
\chi_1 (3, 4) &= \frac{i}{\sqrt{2}} \left[ \alpha(3) \alpha(4) \right] \\
\chi_o (3, 4) &= \frac{i}{\sqrt{2}} \left[ \alpha(3) \beta(4) + \alpha(4) \beta(3) \right] \\
\chi_{-1} (3, 4) &= \frac{i}{\sqrt{2}} \left[ \beta(3) \beta(4) \right]
\end{align*}
\]
where \( \alpha \) and \( \beta \) are the electron spin coordinates. The electronic functions combine in a collision to form the states \( ^3\Sigma_g \) and \( ^3\Sigma_u \). The molecular wave functions are linear combinations of the product functions \( \Psi_A^{(1, 2)} \Phi_B^{(3, 4)} \) and all permutations among the four electrons. Thus, define
\[
\Psi_{I}^{M_s} = \frac{1}{\sqrt{N}} \sum_{p} (-1)^p \mathcal{P}_{1234} \tau_A (1, 2) \Phi_B^{M_s} (3, 4)
\]
and
\[
\Psi_{II}^{M_s} = \mathcal{P}_{AB} \Psi_{I}^{M_s}
\]
where \( \mathcal{P}_{1234} \) is an operator which permutes the electrons. The sum is taken over all possible permutations. \( \mathcal{P}_{AB} \) interchanges the nuclei \( A \) and \( B \). We then have
\[
\sum_{g} \frac{1}{\sqrt{2}} \left( \Psi_{I}^{M_s} + \Psi_{II}^{M_s} \right) = \Psi_s^{M_s} \quad \text{(symmetric)}
\]
\[
\sum_{u} \frac{1}{\sqrt{2}} \left( \Psi_{I}^{M_s} - \Psi_{II}^{M_s} \right) = \Psi_a^{M_s} \quad \text{(antisymmetric)}
\]
for the six molecular states. \( \Psi_s^{M_s} \) and \( \Psi_a^{M_s} \) are the stationary states of the molecule having energy \( E_s \) and \( E_a \) respectively.

In general the wave function which represents the approach of two atoms adiabatically will be a linear time dependent combination of the two stationary states. Since these states have very different energies the two states will evolve at different rates; a phase difference will develop between them vis:
\[ \varphi_{SA} = \int \frac{E_0 - E_a}{\hbar} \, dt \]

where the integral is taken over the collision duration.

We will now consider various pairs of initial states for the colliding atoms and calculate the probabilities of occurrence for the final states.

\[ \Psi_{\text{initial}} = \tilde{\chi}^A_0 \ a(A) \chi^B_1 \ a(B) \quad F = \frac{1}{2} \quad M_{F_1} = \frac{1}{2} \quad E = \frac{3}{2} \quad M_{F_2} = \frac{3}{2} \]

\[ = a(A)a(B)\frac{1}{2} \left[ \left( \tilde{\chi}^A_0 \chi^B_1 + \tilde{\chi}^B_0 \chi^A_1 \right) + \left( \tilde{\chi}^A_0 \chi^B_1 - \tilde{\chi}^B_0 \chi^A_1 \right) \right] \]

\[ \Psi_{\text{final}} = a(A)a(B)\frac{1}{2} \left[ \left( \begin{array}{c} \chi^A_0 \ a(A) \chi^B_1 \ a(B) \\ \chi^B_0 \ a(B) \chi^A_1 \ a(A) \end{array} \right) + e^{i\phi_{SA}} \left( \begin{array}{c} \chi^A_0 \ a(A) \chi^B_1 \ a(B) \\ \chi^B_0 \ a(B) \chi^A_1 \ a(A) \end{array} \right) \right] \]

\[ = \frac{1 + e^{-i\phi} \tilde{\chi}^A_0 \ a(A) \chi^B_1 \ a(B)}{2} + \frac{1 - e^{-i\phi} \tilde{\chi}^B_0 \ a(B) \chi^A_1 \ a(A)}{2} \]

Thus, we find that there are equal probabilities for the occurrence of the final states \( \tilde{\chi}^A_0 \ a(A) \chi^B_1 \ a(B) \) and \( \tilde{\chi}^B_0 \ a(B) \chi^A_1 \ a(A) \).

<table>
<thead>
<tr>
<th>Final States</th>
<th>( F_1 )</th>
<th>( M_{F_1} )</th>
<th>( F_2 )</th>
<th>( M_{F_2} )</th>
<th>Probability</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \frac{1}{2} )</td>
<td>( \frac{1}{2} )</td>
<td>( \frac{3}{2} )</td>
<td>( \frac{3}{2} )</td>
<td>( \frac{1}{2} )</td>
</tr>
<tr>
<td></td>
<td>( \frac{1}{2} )</td>
<td>( \frac{1}{2} )</td>
<td>( \frac{1}{2} )</td>
<td>( \frac{1}{2} )</td>
<td>( \frac{1}{2} )</td>
</tr>
</tbody>
</table>
Initial States  \( F_1 = \frac{1}{2}, M_{F_1} = \frac{1}{2}; \quad F_2 = \frac{3}{2}, M_{F_2} = \frac{1}{2} \)

\[
\Psi_{\text{initial}} \sim \chi_0^A a(A) \left[ \sqrt{\frac{3}{2}} \chi_1^B a(B) + \sqrt{\frac{1}{2}} \chi_1^B b(B) \right]
\]

\[
= a(A) a(B) \frac{1}{2} \sqrt{\frac{3}{2}} \left[ \left( \chi_0^A \chi_1^B + \chi_0^A \chi_1^A \right) + \left( \chi_0^A \chi_1^B - \chi_0^A \chi_1^A \right) \right]
\]

\[
+ a(A) b(B) \frac{1}{2} \sqrt{\frac{1}{2}} \left[ \left( \chi_0^A \chi_1^B + \chi_0^A \chi_1^A \right) + \left( \chi_0^A \chi_1^B - \chi_0^A \chi_1^A \right) \right]
\]

\[
\Psi_{\text{final}} = a(A) a(B) \frac{1}{2} \sqrt{\frac{3}{2}} \left[ \right] + e^{i\phi} \left[ \right]
\]

\[
+ a(A) b(B) \frac{1}{2} \sqrt{\frac{1}{2}} \left[ \right] + e^{i\phi} \left[ \right]
\]

\[
\Psi_{\text{final}} = \frac{1 + e^{i\phi}}{2} \chi_0^A a(A) \left[ \sqrt{\frac{3}{2}} \chi_1^B a(B) + \sqrt{\frac{1}{2}} \chi_1^B b(B) \right]
\]

\[
+ \frac{1 - e^{i\phi}}{2 \sqrt{3}} \chi_0^A b(B) \left[ \chi_1^A a(A) \right]
\]

\[
+ \frac{1 - e^{i\phi}}{3} \chi_0^B a(B) \left[ \sqrt{\frac{3}{2}} \chi_1^A a(B) + \sqrt{\frac{1}{2}} \chi_1^A b(A) \right]
\]

\[
+ \frac{1 - e^{i\phi}}{2 \sqrt{3}} \chi_0^B a(B) \left[ \sqrt{\frac{3}{2}} \chi_1^A a(A) - \sqrt{\frac{1}{2}} \chi_1^A b(A) \right]
\]
Thus:

<table>
<thead>
<tr>
<th>Initial</th>
<th>$F_1$</th>
<th>$M_{f_1}$</th>
<th>$F_2$</th>
<th>$M_{f_2}$</th>
<th>Probability</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{3}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>—</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Final</th>
<th>$\frac{1}{2}$</th>
<th>$\frac{1}{2}$</th>
<th>$\frac{3}{2}$</th>
<th>$\frac{1}{2}$</th>
<th>$\frac{13}{18}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{1}{2}$</td>
<td>$-\frac{1}{2}$</td>
<td>$\frac{3}{2}$</td>
<td>$\frac{3}{2}$</td>
<td>$\frac{3}{18}$</td>
<td></td>
</tr>
<tr>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{2}{18}$</td>
<td></td>
</tr>
</tbody>
</table>

The scattering amplitudes for other pairs of initial states are found in the same manner. The final results are shown in Table II.
APPENDIX C: RELATIONSHIP BETWEEN GROUND
STATE POLARIZATION AND METASTABLE EXPECTATION VALUES

There are several quantities which can be utilized to provide further insight into the optical pumping exchange process. The total polarization of an ensemble of atoms in the states characterized by the quantum number $F$ is

$$ P_F = \frac{1}{F} \sum_i \frac{n_i}{n} \langle F_z \rangle_i \quad \text{and} \quad P_{\text{TOTAL}} = P_{F_z} y + P_{F_y} z $$  \hspace{1cm} (1c)

The electronic spin polarization is

$$ P_E = \frac{1}{S} \sum_i \frac{n_i}{n} \langle S_z \rangle_i $$ \hspace{1cm} (2c)

and the nuclear spin polarization is

$$ P_N = \frac{1}{I} \sum_i \frac{n_i}{n} \langle I_z \rangle_i $$ \hspace{1cm} (3c)

For a state $|F, M\rangle$ described by the quantum numbers $F = I + S$ and $M_F = \langle F_z \rangle$ we can find

$$ \langle I_z \rangle_{F, M} = \langle F, M | I_z | F, M \rangle $$

$$ \langle S_z \rangle_{F, M} = \langle F, M | S_z | F, M \rangle $$

$$ \langle F_z \rangle_{F, M} = \langle F, M | F_z | F, M \rangle = M_F $$

The matrix elements of an operator $\hat{U}$ which satisfy the commutation relations $(\hat{K} \times \hat{U})_m = i \hat{U}_m$ where $\hat{K}$ is an angular momentum operator are given by
\[(\alpha' \kappa m' | \bar{U} | \alpha \kappa m) = \frac{(\alpha' \kappa | \bar{K} \cdot \bar{U} | \alpha \kappa) (Km' | \bar{K} | km)}{K(K+1)}\]

We have, therefore

\[\langle S_z \rangle = (F, M | S_z | F, M) = \frac{(F, M | \bar{S} \cdot \bar{F} | F, M) M_\gamma}{F(F+1)}\]

\[S \cdot F = \frac{1}{2} \left[ |F|^2 - |I|^2 + |S|^2 \right]\]

\[\langle S_z \rangle = \frac{M_\gamma}{2F(F+1)} \left[ F(F+1) - I(I+1) + S(S+1) \right]\]

Similarly:

\[\langle I_\alpha \rangle = \frac{M_\gamma}{2F(F+1)} \left[ F(F+1) - S(S+1) + I(I+1) \right]\]

\[\langle S_z \rangle + \langle I_\alpha \rangle = \frac{M_\gamma}{2F(F+1)} \cdot 2F(F+1) = M_\gamma\]
\[
\begin{array}{cccc}
\langle F_x \rangle & \langle I_z \rangle & \langle S_z \rangle \\
F_x = \frac{1}{2} & n_4 & \frac{1}{2} & -\frac{1}{6} & \frac{2}{3} \\
 & n_5 & -\frac{1}{2} & \frac{1}{6} & -\frac{2}{3} \\
F_x = \frac{-3}{2} & n_4 & \frac{3}{2} & \frac{1}{2} & 1 \\
 & n_3 & \frac{1}{2} & \frac{1}{6} & \frac{1}{3} \\
 & n_2 & -\frac{1}{2} & -\frac{1}{2} & -\frac{1}{3} \\
 & n_1 & -\frac{3}{2} & -\frac{1}{2} & -1 \\
\end{array}
\]

Substituting these expectation values in Eqs. (1c), (2c), and (3c) we find,

\[
P_{F_x = \frac{1}{2}} = \left( \frac{n_4}{n} - \frac{n_5}{n} \right) + \frac{1}{3} \left( \frac{n_3}{n} - \frac{n_2}{n} \right)
\]

\[
P_{F_x = \frac{-3}{2}} = \left( \frac{n_4}{n} - \frac{n_5}{n} \right)
\]

and

\[
P_F = \left( \frac{n_4}{n} - \frac{n_5}{n} \right) + \left( \frac{n_3}{n} - \frac{n_2}{n} \right) + \frac{1}{3} \left( \frac{n_3}{n} - \frac{n_2}{n} \right)
\]

With spin exchange \(n_2 = n_5\) and \(n_3 = n_6\)
So
\[ P_r = \left( \frac{n_4}{n} - \frac{n_1}{n} \right) - \frac{4}{3} \left( \frac{n_3}{n} - \frac{n_2}{n} \right) \]

The electronic polarization is
\[ P_e = \left( \frac{n_4}{n} - \frac{n_1}{n} \right) + \left( \frac{n_3}{n} - \frac{n_2}{n} \right) \]

The metastable nuclear polarization is
\[ P_N = \left( \frac{n_4}{n} - \frac{n_1}{n} \right) \]

Utilizing Eq. (16), for the population densities with spin exchange we find that \( P_N = P_N \) i.e., the nuclear spin polarization of the metastable system is identical with the nuclear polarization of the ground state. Consequently, we might view the spin exchange process continuing until the metastable and ground state nuclear polarizations are equal.
APPENDIX D: NUCLEAR MAGNETIC RESONANCE AT LOW PRESSURES

At a magnetic field of 200 gauss the Boltzmann distribution leads to a He$^3$ nuclear polarization of $10^{-7}$ at 300°K. At a pressure of 1 mm the number of excess spins in the lower state is on the order of $3 \times 10^9$ cm$^{-3}$. Even with fairly large samples this number is hopelessly small to permit observation by NMR. The application of the optical pumping technique provides a polarization enhancement of approximately 6 orders of magnitude resulting in more than $10^{15}$ excess spins in the lower state; a sufficiently large number to be observed experimentally in samples of 65 cm$^3$. This is comparable to the number of excess aligned spins in liquid samples; a fact which provides a convenient method of reference for measurements of polarization.

The observation of the NMR signal in a low pressure gas provides some unique problems which arise as a consequence of the very long relaxation times of the nuclear spin system and the fact that the atoms can move over fairly large distances as the NMR signal is observed.

There are two passage conditions which we wish to consider. The first is called "slow" passage and refers to the condition in which the spin system always remains in an equilibrium condition with the lattice. The area under a slow passage absorption resonance is determined by the effective number of absorbing spins in the sample. The conditions for slow passage are that the applied resonant field $H_1$ must be much less than $1/\sqrt{2} T_1 T_2$ and the passage through resonance $dH_0/dt$ must be much less than the resonance line width. These conditions are patently not satisfied since both $T_1$ and $T_2$ in the gas are very long. A compromise is reached by adjusting the sweep rate and the resonant field until the
transient effects produced are at a minimum. Figure 26 is a recording of the resonance obtained when the slow passage conditions are incompletely satisfied. Figure 27a is a recording of the He$^3$ resonance when the transient effects are minimized. Slower sweep speeds result in a saturation of the resonance (Fig. 27b). The resonance line for a water sample is shown in Fig. 27c. The resonance width is determined by the field gradients. In the case of a low pressure gas the rapid thermal motion of the atom over the container narrows the resonance because it allows the spin to sample many fields some of which cause the precessional frequency to speed up and others to slow it down. The dephasing takes place by a random walk of small steps and the resonance line width is "motionally" narrowed. This motional narrowing depends upon the distance the spin can diffuse during the time taken to traverse the resonance.

For the condition under which the NMR resonance was usually observed the motional narrowing was incomplete. This effect is illustrated in Fig. 28. Here the observed line width is plotted as a function of pressure.

The second passage condition of interest is adiabatic fast passage which involves an inversion of the level populations. The adiabatic condition is satisfied by \( \frac{dH_o}{dt} \ll \gamma H_1^2 \). However, again the ability of the spins to diffuse over large distances and sample a variety of field intensities means that the spin will see the resonant field for only a small fraction of the time. The time a fixed spin would spend on the resonance is \( (\gamma H_1)^{-1} \). If the spin diffuses through a gradient which exceeds \( (\gamma H_1)^{-1} \), then it will no longer be resonant, i.e., the effective \( H_1 \) is reduced by a factor on the order of \( \tau/\tau_o \) where \( \tau = (\gamma H_1)^{-1} \) while \( \tau_o \) is the time required for the spin to diffuse a distance \( \Delta H_o = H_1 \). Consequently the adiabatic condition becomes \( \frac{\Delta H_o}{\tau_o} \ll \gamma H_1^2 \). One is
NMR Transient Effects

.04 cps sweep

.08 cps sweep

1 sec

.12 cps sweep

1 mm sample

Fig. 26 Transient effects as a result of excessive sweep speed. The sweep speed increases from top to bottom.
Fig. 27 NMR line shapes.
Fig. 28 Relative line width vs pressure for $\text{He}^3$ NMR signal. The line width without "motional" narrowing is 20. As the pressure increases the motion of the atom during the resonance line width is reduced.
faced with the difficulty of sweeping through the line in a time sufficiently short to prevent the spins from diffusing a large distance and at the same time providing a sufficiently large $H_1$ to satisfy the adiabatic passage conditions. But as $H_1$ is increased the gradients in $H_1$ can contribute to the relaxation process and the He$^3$ polarization can be quickly destroyed. These competing effects are demonstrated in Fig. 29. The parameter $\alpha$ is defined as the adiabaticity and is measured in terms of the degree of population inversion which occurs. The results are explained in terms of the preceding arguments. In the upper diagram curve A corresponds to increasing efficiency of population inversion as $H_1$ is increased. Curve B represents the relaxation introduced by the gradients according to the theory in Sec. II. C is the resultant curve obtained. The experimental curves in the lower diagrams show the results obtained for the efficiency of the population inversion for a number of sweep rates.
Fig. 29  The adiabaticity $\alpha$ as a function of the strength of the resonant field for different sweep rates. The upper diagram suggests the contributing factors which lead to the experimental curves in the lower diagram.
APPENDIX E: RELAXATION DUE TO SPIN EXCHANGE, $\tau_2$ AND $T_2$

If the spin exchange mechanism dominates the pumping process $\tau_2$ and $T_2$ characterizes the principal source of relaxation for the metastable and ground spin systems. Consequently, the resonance line shapes can be utilized to obtain a measure of $\tau_2$ and $T_2$.

The resonance line shape of the metastable atoms can be observed optically by applying a weak oscillatory magnetic perpendicular to the external dc magnetic field at the Larmor frequency of the metastable atoms. The $g$ value for a state of resultant angular momentum $F$ composed of electronic $J$ and nuclear $I$ is

$$g(F) = g(J) \frac{F(F+1) + J(J+1) - I(I+1)}{2F(F+1)}$$

where $g(J)$ is the splitting factor in the absence of $I \cdot J$ coupling (i.e., no hyperfine interaction) and $g(J) = 2$ for $L = 0$. The energy separation $\Delta E$ between adjacent energy levels of the same $F$ manifold is then

$$\Delta E = g(F) \mu_B H_0$$

where $\mu_B$ = Bohr magneton ($e\hbar/2mc$). For the $F = 3/2$ level we have $g(F) = 4/3$, and for $F = 1/2$ we find $g(F) = 8/3$. The splitting in frequency units for $g = 2$ is $2.8 \times 10^6$ sec$^{-1}$ gauss$^{-1}$. Thus, the resonance of the $2^3S_1$ ($F = 3/2$) atom occurs at $1.9 \times 10^6$ cps in a 1 gauss field and at $3.8 \times 10^6$ cps for the $2^3S_1$ ($F = 1/2$) atom.

The line width is traced out by the variation of the transmitted light as the frequency of the oscillatory magnetic field is varied while the magnetic field is fixed. A trace of the two metastable resonances
obtained in this way is shown in Fig. 4. The full width of the resonance in frequency units, \( \Delta \nu \), at the half-height points of a Lorentzian line is given by

\[
\Delta \nu = \frac{1}{\pi \tau}
\]

where \( \tau \) is the 'coherence' time of the precessing magnetization of the metastable spin system. The quantity \( \tau \) is given by

\[
\frac{1}{\tau} = \frac{1}{\tau_p} + \frac{1}{\tau_e} + \frac{1}{\tau_2}
\]

In the limit of strong spin exchange \( 1/\tau_2 \) dominates and is simply related to the line width of the metastable resonance. Typically, at room temperature and 1 Torr sample pressure \( \tau_2 \) is on the order of \( 10^{-7} \) seconds. This method has been used by Colegrove, Schearer, and Walters \(^{26}\) to obtain the temperature dependence of \( \tau_2 \). The results they obtained indicated that the exchange cross section goes to zero as the temperature goes to absolute zero. This experiment provided the first direct experimental verification of the existence of a long range repulsive interaction between the ground state and metastable state He atoms postulated by Buckingham and Dalgarno. \(^{77}\)

The inverse process \( (T_2)^{-1} \) is a measure of the frequency with which a ground state atom undergoes an exchange collision with the metastable atoms. When the spin-exchange mechanism dominates; perturbations applied to the ground state spin system appear as changes in the metastable populations and hence transmitted light intensity changes. The ground state resonance can be scanned in a manner similar to that employed above by applying an oscillatory magnetic field at the precession frequency of the
ground state atoms. The line width $\Delta \nu$ is related to the relaxation time by

$$\Delta \nu = \frac{1}{\pi T}$$

where $1/T = 1/T_2 + 1/T_r$. Experimentally at room temperature the condition $T_2 \ll T_r$ is always found to be true with the discharge on. Thus the line width is a measure of $T_2$. There is some difficulty associated with the measurement of $T_2$ in this manner. The applied perturbation destroys a fraction of the polarization (the only way it can be observed optically) as the transmitted light changes. However, the light transmitted cannot return to its original intensity faster than $T_p$, the polarization pumping time. So, unless the resonance line is traversed very slowly the resonance line shape will be distorted.

Other optical methods are available as discussed in Ref. 18 for measuring $T_2$. If the exchange time is sufficiently short (i.e., shorter than the Larmor period of the ground state atoms), perturbations applied to the ground state spin system can be observed optically. In particular, Fig. 9 of Ref. 18 shows the response of the optical signal to the sudden application of an oscillatory magnetic field at the nuclear Larmor frequency. In the reference frame rotating at this frequency, the macroscopic magnetization begins to precess about $H_1$, the applied oscillating magnetic field, becoming first parallel, then anti-parallel to the direction of the light beam. The strong exchange coupling forces a change in the populations of the metastable states and produce intensity fluctuation in the light beam. The macroscopic moment at the same time decreases exponentially as the individual moments lose their "coherence." The resultant signal has the form where $2/\theta = 1/T_2 + 1/T_r$. 
The envelope decays exponentially giving a measure of $\theta$. For $T_r \gg T_2$ we can determine $T_2$. This technique was utilized by Greenhow\textsuperscript{23} for measurements of $T_2$. A disadvantage of this method is that gradients in $H_1$ contribute to the line width and can obscure $T_2$ measurements.

The most satisfactory method of determining $T_2$ is the use of a 'crossed-beam' patterned after the development of Bell and Bloom.\textsuperscript{79} Here a second light beam at right angles to the dc field $H_0$ monitors the magnetization in the X-Y plane. A weak $H_1$ normal to $H_0$ at the resonant Larmor frequency of the ground state provides a small amount of coherence to the ordinarily random phases of the precessing moments and results in a nonzero magnetization rotating in the X-Y plane. Again the light beam is modulated but this time at the nuclear spin frequency. If the frequency of $H_1$ is varied through resonance, the line shape can be determined from the variation of the light intensity reaching the detector. Figure 2 of Ref. 30 shows the demodulated output of the detector obtained in this way.

Conventional NMR can also be utilized to obtain directly the ground state resonance width. However, in this case the slow passage results are complicated by the long times encountered rendering the signal intensity too weak to be useful. All the methods are influenced by the presence of field gradients. The rapid diffusion of the spins in the low pressure gas is capable of averaging out the gradients provided the gradient width is small compared to the inverse diffusion time $\gamma \Delta H < 1/\tau_d$. This can easily be satisfied for normal gradients in the laboratory field due to the earth's magnetism; however, the NMR requires considerably higher field (~ 220 G) and the gradients produced by the solenoid were sufficiently large to make the 'motional narrowing' incomplete.
APPENDIX F: CALCULATION OF ION-MOLECULE AND
MOLECULE-MOLECULE REACTION RATES

Theory

The center of mass motion of two particles interacting through a
potential $V(r)$ can be obtained by considering a particle of mass
$M_r = M_1 M_2 / (M_1 + M_2)$ to be scattered by a force center fixed in the CM frame.
For any point along the trajectory shown in Fig. 30 we can write

$$\frac{1}{2} M_r V_o^2 = \frac{1}{2} M_r (r^2 + r^2 \dot{\theta}^2) + V(r)$$

$$M_r b V_o = M_r r^2 \dot{\theta}$$

from which we can find

$$\frac{dr}{d\phi} \frac{d\phi}{dt} = \pm \frac{r^2}{b} \left[ 1 - \frac{V(r)}{M_r V_o^2/2} - \frac{b^2}{r^2} \right]^{1/2}$$

At the distance of closest approach $r_a$, $dr/d\phi = 0$ so that

$$1 - \frac{V(r)}{M_r V_o^2/2} - \frac{b^2}{r^2} = 0$$

This equation defines a relationship between the impact parameter $b$ and
the distance of closest approach $r_a$.

For attractive potentials the orbits of the trajectory can meaning-
fully be classified as spiraling or nonspiraling. For a nonspiraling orbit
the particle approaches the force center, is deflected, and moves on with
Fig. 30 Scattering diagram in the CM reference frame.

**r_a** DISTANCE OF CLOSEST APPROACH

**M_r** REDUCED MASS

**v_o** RELATIVE VELOCITY

**b** IMPACT PARAMETER

CENTER OF MASS SYSTEM
no discontinuities in its motion. There will be, however, some combination of velocity and impact parameter which will cause the particle to spiral into the force center. A cusp appears in the trajectory when the particle is reflected from the hard core. Equation (3F) provides a relationship between the impact parameter \( b \) and the distance of closest approach \( r_a \) for a nonspiraling trajectory only. For values of \( b \) less than same value \( b_{\text{min}} \) there are no solutions to Eq. (3F). This implies that there is no solution for which \( dr/d\tilde{e} = 0 \), i.e., there is no parameter that can be regarded as a distance of closest approach. These correspond to spiraling trajectories. We wish to find that value of \( b = b_{\text{min}} \) such that for \( b < b_{\text{min}} \) we have spiraling trajectories and \( b > b_{\text{min}} \) nonspiraling trajectories. Thus, setting \( d/dr(b^2) = 0 \) we find

\[
1 - \frac{2V(r)}{MrV_0^2} = \frac{r}{MrV_0^2} \frac{dV(r)}{dr} \frac{1}{MrV_0^2} = 0
\]  

(4F)

Equations (3F) and (4F) enable one to solve then for \( b_{\text{min}} \).

If we now suppose that there exists a critical radius \( r_c \) such that the interacting pair approaching each other within this distance will be certain to undergo the reaction under consideration and be impossible at larger distances, we can define a cross section \( \sigma = \pi b_{\text{min}}^2 \). If \( r_c \) lies between 0 and \( r_a \) for \( b_{\text{min}} \), then any collision for which \( b < b_{\text{min}} \) will result in a reaction. A similar type of analysis has been used by Gioumousis and Stevenson to calculate ion-molecule reaction rates.

**Van der Waal's Interaction**

If we assume that the Van der Waal's force is the major source of interaction in the region considered, we can calculate a cross section as follows:
We have $V(r) = -cr^{-6}$ and find that the minimum distance of closest approach for a nonspiral trajectory is

$$r_{\text{min}} = \left(\frac{4C}{MrV_0^2}\right)^{\frac{1}{6}} \quad \text{and} \quad b_{\text{min}} = \sqrt{\frac{3}{2}} \left(\frac{4C}{MrV_0^2}\right)^{\frac{1}{6}}$$

Thus, if $r_c$ lies between 0 and $\sqrt{2/3} b_{\text{min}}$, a reaction is certain to occur. The cross section is then given by

$$\sigma(V_0) = \pi b_{\text{min}}^2 = \frac{3\pi}{2} \left(\frac{4C}{MrV_0^2}\right)^{\frac{1}{3}}$$

**Polarization Interaction**

The calculation for a polarization force between an ion and a molecule has been carried out by Gioumousis and Stevenson. The result is

$$\sigma_p(V_0) = 2\pi \left(\frac{\alpha e^2}{MrV_0^2}\right)^{\frac{1}{2}}$$

where $e$ is the electronic charge and $\alpha$ is the polarizability of the molecule.

**Evaluations of Cross Sections**

The polarizability of He can be obtained from the dielectric constant of He gas and we find $\alpha_p (R.T.) \sim 4 \times 10^{-15}$ cm$^2$. The Van der Waal's constants for various neutral pairs of atoms in inert gases are summarized by Kingston. The constant for the metastable molecule-ground state atom in He is not known. However, a reasonable estimate for $\alpha$ is $\sim 10^{-60}$ cgs
units. This leads to a cross section $\sigma(\text{R.T.}) \sim 5 \times 10^{-16} \text{ cm}^2$, approximately an order of magnitude smaller than the reaction cross section for the molecular ion-ground state pair.
APPENDIX G: CORRELATION FUNCTIONS AND SPECTRA

Consider first a random stationary process which is represented by the quantity $y(t)$ whose average value is zero. The stationarity requires that the average value

$$\left< y(t_0) y(t_0+t) \right>_{\text{AVE } t_0} = \lim_{T \to \infty} \frac{1}{T} \int_{-\infty}^{\infty} y(t_0) y(t_0+t) \, dt_0$$  \hspace{1cm} (1G)

be a function of $t$ alone; that is, the properties of the ensemble described by $y(t_0)$ are independent of the absolute origin of time and depend only on the various time differences between observations. Thus,

$$\left< y(t_0) y(t_0+t) \right>_{\text{AVE } t_0} = \rho_{yy}(t)$$  \hspace{1cm} (2G)

It also follows that

$$\frac{d}{dt} \left< y(t_0) y(t_0+t) \right> = \left< y(t_0) \dot{y}(t_0+t) \right> = -\left< \ddot{y}(t_0) y(t_0+t) \right>$$  \hspace{1cm} (3G)

or

$$\frac{d \rho_{yy}}{dt} = \rho_{y\dot{y}} = -\rho_{\ddot{y}y}$$

and

$$\frac{d^2}{dt^2} \left< y(t_0) y(t_0+t) \right> = \left< y(t_0) \ddot{y}(t_0+t) \right> = -\left< \dddot{y}(t_0) y(t_0+t) \right>$$  \hspace{1cm} (4G)

or

$$\frac{d^2 \rho_{yy}}{dt^2} = \rho_{y\dddot{y}} = -\rho_{\dddot{y}y}$$
Continuing this process one can derive relationships for the correlation functions $\rho_{yy}$ and the cross correlation functions $\rho_{yy}$ and $\rho_{yy}$ in terms of derivatives of $\rho_{yy}$. Thus,

$$\langle y(t_0) \dot{y}(t_0+t) \rangle = - \langle \ddot{y}(t_0) \dot{y}(t_0+t) \rangle$$

$$\rho_{y\dot{y}} = - \rho_{\dot{y}y}$$

and

$$\rho_{y\ddot{y}} = \rho_{\dot{y}\dddot{y}}$$

$$\frac{d\rho_{y\ddot{y}}}{dt^4} = \rho_{y\dddot{y}} \quad (56)$$

The spectral density $G(w)$ of the correlation function $\rho(t)$ is defined as

$$G(w) = 4 \int_0^\infty \rho(t) \cos w t \, dt \quad (66)$$

Upon taking the Fourier transform one gets:

$$\rho(t) = \frac{i}{2\pi} \int_0^\infty G(w) \cos wt \, dw \quad (76)$$

That is, the correlation function of a stationary stochastic (real) process and the spectral density function are each other's cosine Fourier transforms.

We are now in a position to evaluate the spectral density functions for the stochastic variables represented by the velocity of a particle undergoing Brownian motion and the displacement of an harmonic oscillator undergoing Brownian motion. For a free particle of mass $m$ the ensemble equation of motion is
\[ m \frac{dU}{dt} + f U = m k(t) \]  \hspace{1cm} (86)

where \( f \) is a friction coefficient and \( m k(t) \) is a fluctuating force whose average value is zero. The usual assumptions regarding \( k(t) \) are that the force acts only for a very short time interval so that its frequency spectrum is essentially "white"; the spectral density is then taken to be uniform over the frequency intervals of interest.

Writing Eq. (8) as

\[ \dot{U}(t_0) + \beta U(t_0) = K(t) \]  \hspace{1cm} (96)

and multiplying it by itself at a time \( t_0 + t \) and taking the time average, we have

\[
\begin{align*}
\langle \dot{U}(t_0) \dot{U}(t_0 + t) \rangle &+ \beta \left[ \langle U(t_0) \dot{U}(t_0 + t) \rangle + \langle \dot{U}(t_0 + t) \dot{U}(t_0) \rangle \right] \\
&+ \beta^2 \langle U(t_0) U(t_0 + t) \rangle = \langle k(t_0) k(t_0 + t) \rangle
\end{align*}
\]

which can be written as

\[ P_{uu}(t) + \beta \left[ P_{uu}(t) + P_{uu}(t) \right] + \beta^2 P_{uu}(t) = \langle k(t_0) k(t_0 + t) \rangle \]  \hspace{1cm} (106)

Utilizing Eqs. (36) and (46) we get

\[ - \frac{d^2 P_{uu}(t)}{dt^2} + \beta^2 P_{uu}(t) = \langle k(t_0) k(t_0 + t) \rangle \]  \hspace{1cm} (116)
From Eq. (6G) we have

\[- \frac{d^2 \rho_{uu}(t)}{dt^2} = \frac{1}{2\pi} \int_0^\infty \omega^2 G(\omega) \cos \omega t \, d\omega\]

We then have for Eq. (11G)

\[
\frac{1}{2\pi} \int_0^\infty \omega^2 G(\omega) \cos \omega t \, d\omega + \frac{\beta^2}{2\pi} \int_0^\infty G(\omega) \cos \omega t \, d\omega = \frac{1}{2\pi} \int_0^\infty \mathcal{B}(\omega) \cos \omega t \, d\omega
\]

(12G)

where \(G(\omega)\) is the spectral density of the ensemble velocity and \(\mathcal{B}(\omega)\) is the spectral density of the fluctuating force giving rise to the Brownian motion. Eq. (12G) then becomes

\[
\omega^2 G(\omega) + \beta^2 G(\omega) = \mathcal{B}(\omega)
\]

or

\[
G(\omega) = \frac{\mathcal{B}(\omega)}{\omega^2 + \beta^2}
\]

(13G)

Then, since \(\langle u(t_0) u(t + t_0) \rangle = \rho(t)\) we have for \(t = 0\), \(\rho(0) = \langle u^2 \rangle\), the mean squared velocity. It follows then that \(\mathcal{B}(\omega) = 4\beta \langle u^2 \rangle\) so that

\[
G(\omega) = \frac{4\beta \langle u^2 \rangle}{\omega^2 + \beta^2}
\]

(14G)

Suppose now that instead of Eq. (9G) we have the equation
\[
\frac{d^2 y}{dt^2} + \beta \frac{dy}{dt} + \lambda^2 y = k(t)
\]

which describes the Brownian motion of a simple harmonic oscillator.

\( y(t) \) is the stochastic variable representing the position of the particle.

Following a procedure identical to the earlier case one can easily show that

\[
\frac{d^4 p_{yy}}{dt^4} + (\beta^2 - 2\lambda^2) \frac{d^2 p_{yy}}{dt^2} + \lambda^4 p_{yy} = \langle k(t_0) k(t_0 + t) \rangle
\]

From which it follows that

\[
G(\omega) = \frac{4\beta \langle u^2 \rangle}{(\omega^2 - \lambda^2)^2 + \beta^2 \omega^2}
\]

where \( G(\omega) \) is the spectral density function of the process representing the displacement of a Brownian oscillator.

The spectral density function for the displacement of a free particle is then found by taking the limit in which the stiffness constant \( \lambda \) approaches zero. Thus

\[
G(\omega)_{\text{free}} = \frac{4\beta \langle u^2 \rangle}{\omega^2 (\omega^2 + \beta^2)}
\]
GLOSSARY OF TERMS (in order of appearance)

$\tau_p$ Metastable pumping time.

$\tau_R$ Metastable relaxation time not due to exchange.

$A_{jk}$ $B_{ik}$ Probabilities for absorption and emission of photons.

$M_f$ z component of total angular momentum.

$\tau_2$ Metastable spin exchange time.

$n$ Metastable density.

$N$ Ground state density.

$T_2$ Ground state spin exchange time.

$P$ Polarization.

$T_p$ Ground state pumping time.

$F$ Total angular momentum.

$I$ Nuclear spin angular momentum.

$J$ Electron spin angular momentum plus orbital angular momentum.

$\langle F_z \rangle$ $M_f$

$a, b, c$ Absorption probabilities for $\sigma^+$ radiation from He$^4$ lamp.

$I_o$ Optical absorption due to unpolarized metastable atoms.

$I$ Optical absorption due to polarized metastable atoms.

$D$ Diffusion coefficient ($cm^2 sec^{-1}$).

$A$ Diffusion length (cm).

$M$ Metastable helium atom.

$\sigma$ Geometric cross section.

$T_e$ Electron temperature.

$T_g$ Gas temperature.

$H$ Magnetic field.

$h(t)$ Fluctuating magnetic field.
Glossary of Terms (continued)

\( \langle \omega \rangle \)  Transition probability per unit time.

\( T_1 \)  Spin-lattice relaxation time.

\( U_y \)  y component of rms velocity.

\( G \)  Magnetic gradient intensity.

\( \tau_c \)  Mean time between atomic collisions.

\( \langle U^2 \rangle \)  Mean squared velocity.

\( \gamma \)  Gyromagnetic ratio.

\( \rho(t) \)  Autocorrelation function.

\( G(\omega) \)  Spectral density function.