SPIN DEPENDENT REACTIONS
IN AN
ELECTRONICALLY EXCITED HELIUM DISCHARGE

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The electron spin dependence of reactions involving helium metastable atoms is investigated using optical pumping and microwave diagnostic techniques.

Wigner (1927) proposed that electron spin angular momentum is conserved in atomic collisions. This rule of electron spin conservation is tested in the collision of two helium triplet metastable atoms in the afterglow of a helium discharge at 2 Torr:

$$\text{He} \left(2^3S_1\right) + \text{He} \left(2^3S_1\right) \rightarrow \text{He} \left(1S_0\right) + \text{He}^+ + e^-$$

If the Wigner spin rule holds, the above reaction will be dependent upon the spin states of the colliding metastable atoms.

A simple theory is developed showing the influence of spin conservation on the number of electrons produced in such reactions. The effect of electrons resulting from other collisions in the afterglow is introduced, and the two treatments are combined to yield a quantitative prediction of the results of experimental observation.

Optical pumping is used to change the normal distribution of the spin states. Microwave diagnostic techniques
are used to observe any corresponding change in the number of electrons in the helium afterglow.

A very definite and measurable change in electron number density results, indicating that the Wigner spin rule holds in the collision of helium triplet metastable atoms. The experimental data lie within 20% of the theoretical predictions in the early afterglow period, with the agreement decreasing at later times.
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I. INTRODUCTION

In 1927 Wigner proposed that total electron spin angular momentum is conserved in a collision involving two gas atoms. Some subsequent experiments have confirmed this conservation rule, while others have shown that exceptions exist. The validity of spin conservation is assumed to account for the measured spin polarization of a beam of electrons in some notable recent work. In general, the spin conservation rule is expected to hold best when the angular momenta of an atom have LS coupling so that we may speak of a total electron spin before and after collision.

The experiment described here furnishes a relatively direct method for testing spin conservation: the reactions are simple and they involve only S states of helium with n=2, where LS coupling is a very good approximation. It extends the work of Stockwell by the adoption of a different sampling technique which permits the use of phase-sensitive detection methods and leads to greater sensitivity of measurement.

The reaction which forms the basis for this experiment is the collision of two helium triplet metastable atoms:

\[ \text{He} (2^3S_1) + \text{He} (2^3S_1) \rightarrow \text{He} (1^1S_0) + \text{He}^+ + e^- \] (1)

This reaction is responsible for most of the electrons produced during the afterglow of a pulsed helium discharge.
The triplet metastable atoms have $S=1$, the ground state atoms have $S=0$ and the ion and electron each have $s=\frac{1}{2}$. In the absence of a magnetic field, the conservation rule would have us list the possibilities for the combination of the two metastable atoms on the left; then we would do a similar analysis for the products on the right. If a possible value of total spin angular momentum on the left coincided with a possible value on the right, the reaction would be permitted.

If we define an axis of quantization, the restrictions implicit in Wigner's rule of spin conservation become more precise. It is the total $z$ component of electron spin which must be conserved. In eq. (1) the $m_j$ of each of the metastable atoms may be $+1$, $0$, or $-1$. The ground state has $m_j = 0$ and the electron and ion may each have $m_j = \pm \frac{1}{2}$.

This experiment hinges on the fact that not every metastable-metastable collision can proceed as shown and at the same time conserve electron spin angular momentum. For example, if two metastables of $m_j = +1$ collide, we have a total $m_j = +2$ on the left. There is no combination on the right that will yield $m_j = +2$. This particular reaction cannot proceed if the conservation of spin angular momentum is valid in this case. The richer the population of $m_j = +1$ states in the sample which contains the reactants, the fewer the reactions that can proceed. Thus, the smaller will be the number of electrons produced in these reactions.
Optical pumping provides a means of enriching $m_j = +1$ (or, alternatively $m_j = -1$) states in the sample. If spin conservation holds, this will prevent some of the metastable-metastable collisions from proceeding as shown. If this enrichment is destroyed, that is, when we go from the "pumped" to the "unpumped" state, more reactions of the type shown will be possible, and there should be an increase in the number of electrons in the sample. It is this increase in electron number density which is measured in the present experiment and is proposed as a direct confirmation of spin angular momentum conservation.

The reaction (1) is one of several types of collision reactions that may take place in a sample of gaseous helium in the period following an active electric discharge. The discharge is pulsed periodically and the interval after active discharge, the "afterglow", is observed. The rapid decay of many of the species present during discharge greatly reduces the number of reactions in the afterglow. Because of detailed studies of helium afterglows$^7$, $^8$, $^9$, we have some confidence as to the types of reactions which produce electrons and which may affect our measurement.

The approach taken to obtain this measurement is of some intrinsic interest since it represents a coincidence of several experimental techniques: optical pumping, microwave methods, and frequency source compensation. Optical pumping enriches the population of $m_j = +1$ triplet metastables,
microwave diagnostic techniques provide a means of measuring electron densities, and source compensation techniques make it possible to measure very small changes in these densities.
II. THEORY

A. Introduction

In order to speak meaningfully of a confirmation of spin conservation, there must be some criterion by which we can judge the results of experiment. In this section we develop those theoretical points upon which the experiment is based and according to which laboratory measurements may be related to a verification of spin conservation.

The theory of optical pumping in $^3$He will first be presented. Since a change in electron number density serves as the crucial part of the experiment, we will investigate the sources of electrons in the sample as well as their time dependence. Finally, since the electron density is not observed directly, its relation to the appropriate laboratory variables will be developed.
B. **Optical Pumping in $^3\text{He}$**

Optical pumping refers to the use of light to achieve a population of a set of energy levels of a system which is different from the normal Boltzmann distribution. In the case of helium, this technique can cause a population redistribution of the magnetic sublevels of the $^2\text{S}_1$ metastable atom. If the helium isotope of mass number three is used, a population redistribution of the hyperfine sublevels of the ground state atoms also occurs through spin exchange with the metastable atoms. This leads to a simple optical technique for measuring the relative populations.

The theory of optical pumping in $^3\text{He}$ has been described in detail in the work of Colegrove, Schearer, and Walters.\textsuperscript{10} A brief summary of that theory is included here for completeness. Figure 1 presents a diagram of the energy levels of $^3\text{He}$ in an external magnetic field. If a weak electric discharge is maintained in a low pressure sample, about one atom in $10^6$ will be in the $^2\text{S}_1$ state, the triplet metastable state. If 1.08 micron resonance radiation traveling in the direction of the magnetic field is incident upon the sample, transitions of the triplet metastable atoms to the $^2\text{P}$ states will be excited, $\Delta L = +1$. When this radiation is right hand circularly polarized, there will be the additional selection rule $\Delta m = +1$. (For left hand circularly polarized light, it would be $\Delta m = -1$.) A further restriction may be placed on the possible transitions if the resonance radiation is derived
Fig. 1 Energy level diagram of $^3$He showing the pertinent levels.
from a lamp containing $^4\text{He}$. The isotope shift is such that the $2^3\text{P}_{1,2} \rightarrow 2^3\text{S}_1$ radiation emitted from the $^4\text{He}$ lamp will excite only $2^3\text{S}_1 \rightarrow 2^3\text{P}_0$ transitions in the $^3\text{He}$ sample.\(^1\)

The $2^3\text{P}_0$ level is split by the magnetic field into $m = \frac{1}{2}$ and $m = -\frac{1}{2}$ components. By applying the selection rules mentioned above, it is seen that there will be only transitions from the $-\frac{1}{2}$ and $-3/2$ sublevels of the $2^3\text{S}_1$ atoms to the $\frac{1}{2}$ and $-\frac{1}{2}$ sublevels of the $2^3\text{P}_0$ atoms. These $2^3\text{P}_0$ sublevels decay with appropriate electric dipole transition probabilities to all the $2^3\text{S}_1$ sublevels, the selection rules being $\Delta m = +1, 0, -1$. Since they are excited with a "bias" of $\Delta m = +1$ but decay without such a "bias", after a time there is a net transfer of the lower magnetic sublevels to higher sublevels. If this net transfer dominates processes which tend to relax the population redistribution, there will be a net depopulation of the lower sublevels in favor of the higher ones. In their paper, Colegrove et al. showed that the rates were such that there could indeed be a population redistribution of these magnetic sublevels. Since there is a net increase of angular momentum and concomitant orientation of magnetic moments, the term "polarization" is used to refer to this type of population redistribution.

The pioneer experiments in $^3\text{He}$ also showed that the ground state atoms ($^1\text{S}_0$) exhibited a polarization. Since the $2^3\text{S}_1$ states were doubly forbidden to decay to the ground state,
the coupling between metastable and ground state atoms was not radiative. The coupling mechanism was shown to be that of the spin-exchange collision of a metastable atom with one in the ground state.\textsuperscript{10} In a dilute gas where there are $10^6$ ground state atoms for every metastable atom, the most likely event for a metastable is a collision with a ground state atom. In such a collision, the metastability may be exchanged. Exchange would have little physical significance if the colliding atoms were in the same nuclear spin state (as they are in $^4$He, for example). In $^3$He there is the possibility that the colliding species are in different spin states. Take, for example, the case where a ground state atom of nuclear spin component $m_I = -\frac{1}{2}$ collides with a metastable atom of nuclear spin component $m_I = +\frac{1}{2}$, and metastability is exchanged. The metastable atom resulting after collision has $m_I = -\frac{1}{2}$ and the ground state atom has $m_I = +\frac{1}{2}$. Thus, the metastability exchange appears as a "spin-flip" of ground state atoms (with resulting spin-flip of the metastable atoms in the opposite sense). If there is a higher population of $m_I = +\frac{1}{2}$ metastables than those with $m_I = -\frac{1}{2}$ and the relaxation rate of the ground state spin system is low enough, there will result a net polarization of the ground state system.

Polarization of ground state atoms is not of direct interest in this experiment since it is a reaction involving triplet metastable atoms that is being studied. In the paper
mentioned above, Colegrove et al. developed a phenomenological theory which related the several rate equations involved in this optical pumping-spin exchange process. They observed experimentally that the relaxation time for ground state polarization was much greater than the characteristic time for the ground state system to approach equilibrium. Using this observation, they showed that the steady state polarizations of ground state and metastable systems are equal. They also showed that depolarizing the ground state system quickly depolarizes the metastable system.

The amount of resonance radiation transmitted through the sample cell decreases on depolarization because there are more available absorbers in the sample. Thus, optical detection techniques may be employed in the measurement of polarization. The ground state atoms are depolarized by applying an oscillating magnetic field at right angles to the direction of the fixed magnetic field that accounts for sublevel splitting. If the frequency of the oscillating field is equal to the Larmor frequency of the ground state atoms, transitions between the $m_j = +\frac{1}{2}$ and $m_j = -\frac{1}{2}$ levels will take place. This mixes the states and destroys polarization. Of course, the Larmor frequency of the metastable atoms might be applied to destroy polarization, but the frequency is three orders of magnitude higher, and for engineering considerations (see below, p. 32) it was necessary to use the ground state depolarization method.
The optical quantities measured in the laboratory are proportional to the intensity of resonance radiation absorbed in the sample cell. If $P$ is the polarization, $I$ the radiation absorbed by the polarized metastable atoms, and $I_0$ the radiation absorbed when the sample is depolarized by saturating the nuclear resonance, Schearer has shown:

$$I_0 - I = \frac{\Delta I}{I_0} = \frac{P}{2P^2 + 6} (11.8 - 3.6P - 0.2P^2)$$

For cases of low polarization ($< 0.1$) $P = \frac{1}{2}(I/I_0)$. This latter formula was used to determine percentage of polarization of metastable atoms in the present experiment.
C. Electron Density in $^3$He Afterglow

During an active electric discharge in gaseous helium, there are present many atomic species, ionic and neutral, excited and ground state. When the excitation that produces the discharge is terminated, the ions and electrons recombine, atoms and electrons collide, and excited states decay, all with characteristic times.

The lifetimes of all species after termination of the discharge is quite short (of the order of microseconds) except for electrons, a corresponding number of ions, and the singlet ($^1S_0$) and triplet ($^3S_1$) metastable atoms. The lifetime of these latter species in this "afterglow" period is limited more by diffusion to the walls and by collision than by radiation.

The reaction which is of primary interest in this experiment is the collision of two triplet metastable atoms:

$$\text{He}(^3S_1) + \text{He}(^3S_1) \rightarrow \text{He}(^1S_0) + \text{He}^+ + e^- \quad (2)$$

The means for investigating this reaction relates to the number density of electrons in the afterglow plasma, so the time dependence of electrons in the afterglow must be examined. This dependence must take into account the electrons left from the active discharge, the diffusion of electrons to the walls, and all production mechanisms which contribute to the number of electrons after the discharge is terminated. In addition to the triplet-triplet collision mentioned above,
there are two others which contribute electrons:

\[ \text{He}(2^3S_1) + \text{He}(2^1S_0) \rightarrow \text{He}(1^1S_0) + \text{He}^+ + e^- \]  

(3)

\[ \text{He}(2^1S_0) + \text{He}(2^1S_0) \rightarrow \text{He}(1^1S_0) + \text{He}^+ + e^- \]  

(4)

1. Metastable and Electron Rate Equations

The differential equation giving the rate of change of triplet metastable concentration is:

\[
\frac{dT}{dt} = D_T v^2 T - v_d T - v_i T - 2\beta T^2 + \alpha N_e S - \gamma TS
\]

where \(T\) is the triplet metastable concentration;

\(D_T\) is the triplet diffusion coefficient;

\(v_d\) is the frequency of volume loss not resulting in ionization;

\(v_i\) is the frequency of destruction processes with impurity atoms yielding ions;

\(\beta\) is the coefficient for the production of an ion from two triplets; (this is related to the cross section for reaction (2) above by: \(\beta = \sigma_1 v\))

\(\gamma\) is the coefficient for singlet-triplet collisions—reaction (4) above;

\(S\) is the singlet metastable concentration;

\(N_e\) is the electron density; and,

\(\alpha\) is the coefficient for singlet to triplet conversion, represented by the reaction:

\[ \text{He}(2^1S_0) + e^- \rightarrow \text{He}(2^3S_1) + e^- + 0.79\text{eV} \]  

(5)
Extending the approach of Biondi\textsuperscript{7}, we neglect the last three terms, consider the first diffusion mode, and arrive at the solution:

\[
T = T_0(\tau) \exp(-\frac{t}{\tau_T})
\]

where \( \tau_T = \frac{D_T}{\Lambda^2} + \nu_d + \nu_i \); \( T_0 = T(r=0, t=0) J_0(j_0, \frac{r}{R}) \cos \frac{\pi Z}{L} \)

\[
\frac{1}{\Lambda^2} = \frac{\pi^2}{L^2} + \frac{(2.4)^2}{(R)^2}
\]

for a cylinder

\( j_0, l \) is the first root of the zeroth order Bessel function.

The singlet concentration is given by:

\[
\frac{dS}{dt} = D_S \nu'^2S - \nu_d'S - \nu_i'S - 2\xi S^2 - \gamma TS - \alpha N_e S
\]

where \( D_S \) is the singlet diffusion coefficient;
\( \xi \) is the coefficient for the singlet-singlet collision; [see eq. (3)]

\( \nu_d' \) & \( \nu_i' \) are frequencies analogous to \( \nu_d \) and \( \nu_i \).

In order to solve this equation, the relative importance of the terms must be examined. For singlets at pressures of 2 Torr, diffusion to the walls and conversion to triplets are comparable in magnitude.\textsuperscript{9} So the last term may not be neglected. \( N_e \) is a function of time, which complicates the solution of the equation.

The approach will be to consider first the diffusion-limited case; i.e., where conversion is neglected. Then
we will investigate the influence of conversion on this solution, using some appropriate average $N_e$.

In the diffusion-limited case:

$$S = S_0(\bar{x}) \exp(-\frac{t}{\tau_s}) \quad \text{(7)}$$

where

$$\frac{1}{\tau_s} = \frac{D_s}{\lambda^2} + v' + v'$$

The electron density time dependence is given by:

$$\frac{dN_e}{dt} = D_e \psi^2 N_e + \beta T^2 + 2\gamma TS + \xi S^2$$

where $D_e$ is the diffusion coefficient for electrons.

In the diffusion-limited case, since triplets and singlets have diffusion coefficients that are approximately equal, the ratio of singlets to triplets is constant, $S = \psi T$. Using this approximation and eqs. (6) and (7), we obtain a lowest mode solution for the electron density:

$$N_e = A \exp(-\frac{t}{\tau_e}) - B \exp(-\frac{2t}{\tau_T}) - C \exp(-\frac{2t}{\tau_s})$$

where $A = N_e(t=0) + B + C$

$$B = \frac{(\beta + \gamma \phi)}{2} \frac{T^2}{\tau_T - \frac{1}{\tau_e}} \quad C = \frac{(\gamma \phi + \xi \phi^2)}{2} \frac{T^2}{\tau_s - \frac{1}{\tau_e}}$$

In this solution, the first term represents the electron density at the time of termination of excitation plus the
contributions from triplet-triplet, triplet-singlet, and singlet-singlet collisions. The second term represents the loss by diffusion of triplets that might have contributed to $N_e$. The last term represents a similar loss for singlets.

With the "killing" pulse (see below, p. 34) which sweeps electrons to the walls, the initial electron density is zero. Setting $N_e(t=0)$ equal to zero and regrouping terms:

$$N_e(t,P) = [\beta(P) + \gamma \phi] T_0^2 g(t) + (\gamma \phi + \xi \phi^2) T_0^2 h(t)$$

where

$$g(t) = \exp\left(-\frac{t}{T_e}\right) - \exp\left(-\frac{2t}{T_e}\right)$$

and

$$h(t) = \exp\left(-\frac{t}{T_s}\right) - \exp\left(-\frac{2t}{T_s}\right)$$

$\beta$ and thus $N_e$ are functions of the polarization if spin conservation holds.

The fractional change in electron density when we go from the polarized to the unpolarized state is:

$$\frac{\Delta N_e(t,P)}{N_e(t,0)} = \frac{\beta(0) - \beta(P)}{\beta(0)} K(t)$$

where

$$K(t) = \left[1 + \frac{2\gamma \phi}{\beta(0)} + \frac{\xi \phi^2}{\beta(0)} \frac{h(t)}{g(t)}\right]^{-1}$$
2. Polarization Dependence

Following Stockwell\(^6\), we consider the triplets in a hypothetical three-level system. We may represent collisions between triplet metastable atoms as

\[
\text{Metastable } \#1 + \text{Metastable } \#2 \rightarrow \text{He} + \text{He}^+ + e^-
\]

\[
S = 1, \quad n_+ = n_-
\]

\[
m_j = \begin{cases} 
+1 & n_+ \to n_+ \\
0 & n_0 \to n_0 \\
-1 & n_- \to n_-
\end{cases}
\]

where \(n_+, n_0, n_-\) are the numbers of triplets in each state.

The solid lines represent combinations of triplet metastables which may react according to eq. (2) without violating spin conservation. The two dashed lines represent spin rule forbidden combinations. Let \(\Gamma\) represent the proportion of possible intercombinations which are spin allowed. \(\Gamma\) is directly proportional to \(\beta\) and the first factor of eq. (8) becomes

\[
1 - \frac{\Gamma_p}{\Gamma_0}
\]

where

\[
\Gamma = \frac{2n_+ n_0 + 2n_0 n_- + 2n_+ n_- + n_0^2}{2n_+ n_0 + 2n_+ n_- + 2n_0 n_- + n_0^2 + n_+^2 + n_-^2}
\]

\[
= \frac{n^2 - n_+^2 - n_-^2}{n^2}
\]

(9)

The three hypothetical levels must be related to the six sublevels of the \(^3\)He triplet metastable atoms.
The duration of the triplet-triplet collision is short (~$10^{-12}$ sec) and the $^3$He nuclei have no time to precess in the magnetic field of the electrons. So we would expect each nucleus to have the same expectation value of $z$ component of nuclear spin before and after the collision. So it is the $z$ component of electron spin which must be conserved according to the Wigner rule of spin conservation.

Stockwell expanded the $|F, m_F\rangle$ eigenfunctions in terms of the $|m_I, m_S\rangle$. He then tabulated the levels together with their makeup according to electron spin, giving the squares of the Clebsch-Gordon coefficients and the expectation value of $S_z$.

$$
\begin{array}{cccccc}
\text{m}_F & \text{m}_S = +1 & 0 & -1 & \langle S_z \rangle \\
F=1/2 & n_6 & 1/2 & 2/3 & 1/3 & 0 & 2/3 \\
& n_5 & -1/2 & 0 & 1/3 & 2/3 & -2/3 \\
F=3/2 & n_4 & 3/2 & 1 & 0 & 0 & 1 \\
& n_3 & 1/2 & 1/3 & 2/3 & 0 & 1/3 \\
& n_2 & -1/2 & 0 & 2/3 & 1/3 & -1/3 \\
& n_1 & -3/2 & 0 & 0 & 1 & -1 \\
\end{array}
$$

By reading the table vertically, we can regard the $^3$He metastables as having three sublevels of electron spin $+1$, $0$, and $-1$ with populations $n_+$, $n_0$, and $n_-$ given by

$$
n_+ = (2/3)n_6 + n_4 + (1/3)n_3
$$
\[ n_0 = (1/3)n_6 + (1/3)n_5 + (2/3)n_3 + (2/3)n_2 \]  
\[ n_- = (2/3)n_5 + (1/3)n_2 + n_1 \]  

Colegrove et al.\(^{10}\) showed that the sublevels are populated so that

\[ \frac{n_1}{n_2} = \frac{n_2}{n_3} = \frac{n_3}{n_4} = \frac{n_5}{n_6} = \frac{N_1}{N_2} = \frac{1-P}{1+P}; \quad n_2 = n_5, \quad n_3 = n_6 \]

If \( \sum_{i=1}^{6} n_i = n \) then the \( n_i \) become

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

Using eq. (11) in eq. (10) gives:

\[ n_+ = n_3 + n_4 = \left[ \frac{(1+P)^2}{3+P^2} \right] n \]
\[ n_0 = n_2 + n_3 = \left[ \frac{(1-P)^2}{3+P^2} \right] n \]
\[ n_- = n_1 + n_2 = \left[ \frac{(1-P)^2}{3+P^2} \right] n \]

And using this in eq. (9) leads to a value for \( \Gamma \) in terms of the polarization:

\[ \Gamma = \frac{(7-6P^2-P^4)}{(9+6P^2+P^4)} \]

\[ \Gamma_0 = 7/9 \] so we can predict the value of \( 1 - \frac{\Gamma \Gamma_0}{\Gamma_0} \) in terms of the measured polarization.
3. Time Dependence of Predicted Shift

The factor $K(t)$ contains the influence of singlet to triplet conversion as well as the diffusion of singlets and triplets. The assumption that spin allowed collisions occur with equal cross section leads to the following values for ratios which appear in $K(t)$:

$$\beta = \frac{7}{9} \quad \gamma = \frac{7}{9} \quad \xi$$

The restriction that $\phi$ be independent of the time is now removed.

$$\phi = \frac{S}{T} = \frac{S_0 \exp[-t(\frac{1}{\tau_s} - \frac{1}{\tau_T})]}{T_0 \exp(-\frac{t}{\tau_T}) + S_0 [1-\exp(-\frac{t}{\tau_T})] \exp(-\frac{t}{\tau_s})}$$

where $\tau_s$ is the diffusion time for singlets; and $\tau_s'$ is the conversion time for singlets.

Using the approximations $\tau_T = \tau_s$ and $S_0 = T_0/3$ gives:

$$\phi = \frac{1}{4 \exp(\frac{t}{\tau_s})-1}$$

To evaluate this factor and the value of $h(t)/g(t)$ appearing in $K(t)$, we must have some notion of the size of $\tau_s$ and $\tau_s'$. The frequency for conversion of singlets to triplets is:

$$\frac{1}{\tau_s'} = N \sigma V$$
For thermal electrons $\bar{v} = 1.2 \times 10^7$ cm/sec; $\sigma = 3 \times 10^{-14}$ cm$^2$, according to Phelps. For $N_e$, we use an average based on the results of measurements in the afterglow (p. 46).

$$N_e = 1.4 \times 10^9 / \text{cm}^3$$

This gives $\frac{1}{\tau_s} = 5 \times 10^2 / \text{sec}$

$$\frac{1}{\tau_s} = 250 / 0.635 = 4 \times 10^2 / \text{sec}$$

Using these, the factor $h(t)/g(t)$ becomes

$$\frac{2}{7} \frac{1 - \exp\left(-\frac{7t}{2\tau_s}\right)}{1 - \exp\left(-\frac{t}{\tau_s}\right)}$$

The factor $K(t)$, using these approximations, is plotted as the "theoretical" curve of Fig. 7.

The fractional change in electron density may now be written

$$\frac{\Delta N_e}{N_e(t,0)} = \left(1 - \frac{\Gamma_p}{\Gamma_0}\right) K(t) \quad (13)$$
D. Frequency Shift of a Cavity Containing a Plasma

The change in electron density predicted in the preceding section is not observed directly. In this section, it will be shown that electron densities are related to the electromagnetic resonant frequencies of enclosures which contain the electrons. If the helium sample is placed in such an enclosure, or "microwave cavity", a change in the electron density within the sample cell will manifest itself as a shift in the cavity's resonant frequency.

A microwave cavity has various characteristic resonant frequencies which correspond to modes of oscillation of an electromagnetic field contained within the cavity. Some of these frequencies may be degenerate; i.e., a resonant frequency may correspond to more than one mode. The cavity also possesses a characteristic quality factor or $Q$ which relates to the amount of energy dissipated per cycle of the electromagnetic oscillation.

If this cavity is made to enclose an electron gas or a plasma both the characteristic resonant frequencies and the quality factor will be perturbed. Slater has investigated this perturbation in great detail. In the case of a small perturbation, he finds, to first order:

$$
\left\{ \frac{1}{Q(t)} - \frac{1}{Q_0} \right\} - 2j \frac{\Delta \omega(t)}{\omega_0} = \frac{1}{\varepsilon_0 \omega_0} \frac{\int (\sigma_r + j \sigma_i) \tilde{E}^2 dV}{\int \tilde{E}^2 dV} \tag{14}
$$
where \( Q \) is the quality factor of cavity;

\( \omega_0 \) is a resonant frequency of the empty cavity;

\( \Delta \omega \) is the change in this resonance;

\( \varepsilon_0 \) is the permittivity of free space;

\( \sigma_r \) is the real part of the conductivity;

\( \sigma_i \) is the imaginary part of the conductivity;

\( \vec{E} \) is the electric field; and

\( dV \) is a volume element of the cavity.

This equation is valid for the case of the electron current much smaller than the displacement current; i.e.,

\[
|\sigma_c| = [\sigma_r^2 + \sigma_i^2]^{1/2} \ll \omega_0 \varepsilon_0 \tag{15}
\]

The conductivity \( \sigma \) which appears in Slater's formulation has been written as explicitly complex, following Oskam.\(^1^4\) This makes manifest the possibility that the current produced by the field \( \vec{E} \) may not be in phase with the field, the 90° out-of-phase component being represented by the imaginary part. An inspection of the terms on the left shows that it is this part which determines the shift in the resonant frequency. It can also be seen that, for cavities of moderately high \( Q \), the perturbation is principally on the resonant frequency.

If the collision frequency of the electrons is much less than the angular frequency of the microwave field \( \vec{E} \), it can be shown\(^1^5\) that the conductivity is almost totally imaginary, the imaginary part being:
\[ \alpha_1(\vec{r}, t) = \frac{-e^2 N_e(\vec{r}, t)}{m \omega_0} \]  

(16)

where \( e \) is the charge of the electron;

\( N_e \) is the electron number density;

\( m \) is the mass of the electron; and

\( \omega_0 \) is the angular frequency of the microwave field.

In order to justify the above assumption, we must examine the collision frequency in the present experiment and compare it to the microwave angular frequency. Collision frequency is given by:

\[ \nu = \bar{v} N q_D \]

where \( \bar{v} \) is the mean velocity of the electrons;

\( N \) is the number density of atoms in the sample; and

\( q_D \) is the cross section for momentum transfer.

Values typical in our case are:

\( q_D \sim 5 \times 10^{16} \text{ cm}^2 \) for thermal electrons in He\(^{14}\)

\( N \sim 6 \times 10^{16} \text{ atoms/cm}^3 \) for pressure of 2 Torr

\( \bar{v} \sim 10^7 \text{ cm/sec} \) for thermal electrons

So \( \nu \sim 3 \times 10^5 \text{/sec} \); the angular frequency of the microwaves used is \( \sim 6 \times 10^{10} \). So our approximation is justified.

The above expression for \( \alpha \), eq. (16) allows to see what restrictions are placed by the approximation eq. (15).

\[ \frac{e^2 N_e(\vec{r}, t)}{m \omega_0} \ll \omega_0 \epsilon_0 ; \quad N_e(\vec{r}, t) \ll 10^{-8} \epsilon^2 \]

For probing frequencies of the order of \( 10^{10} \text{ Hz} \), this requires
that $N_e(\vec{r}, t) \ll 10^{12}$, a condition which is certainly met in the present experiment. Using eq. (16), we may write the imaginary part of eq. (14):

$$\Delta \omega(t) = \frac{e^2}{2 \varepsilon_0 \omega_0^2 m} \int \frac{N_e(\vec{r}, t) \vec{E}^2 dV}{\vec{E}^2 dV}$$

(17)

The factor containing the integrals depends upon the spatial distribution of the electrons and the electric field. Oskam has evaluated this factor for a number of different geometries and modes. For the present experiment, we need only the results for a cylindrical cavity in the $TE_{011}$ mode. Here we rely heavily on Oskam's treatment as presented by Stockwell.

Consider the origin of a cylindrical coordinate system in the center of a cylindrical cavity of radius $R_1$ and length $L_1$ with the $z$ axis along the cavity axis. In the $TE_{011}$ mode the field is:

- $E_r = 0$
- $E_z = 0$
- $E_{\phi} = \frac{E_0}{J_1[j_{1,1} \frac{r_{\text{max}}}{R_1}]} J_1[j_{1,1} \frac{r}{R_1}] \cos\left(\frac{\pi z}{L_1}\right)$

where $j_{1,1}$ is the first zero of $J_1$;

$r_{\text{max}}$ is the value of $r$ for which $J_1$ has its first maximum and thus normalizes the field to $E_0$.

Then the denominator becomes:

$$\int E^2(\vec{r}) dV = \frac{\pi}{2} \left[ \frac{J_0[j_{1,1}]}{J_1[j_{1,1} \frac{r_{\text{max}}}{R_1}]} \right]^2 L_1 R_1^2 E_0^2$$
For the numerator, it is necessary to know the distribution of electrons. If the electrons are in the first diffusion mode in a cylindrical container,

\[ N_e(r, t) = N_{e0}(t) J_0 \left( j_1, 0, \frac{r}{R} \right) \cos \left( \frac{\pi z}{L} \right) \]

where the cylinder has radius \( R \) and length \( L \). Using these, Oskam shows that the integral factor in eq. (17) is

\[ \left( j_1, 1 \right)^2 N_{e0}(t) \left\{ \frac{1 + \cos(\pi \ell)}{1 - 4\ell^2} \right\} D_1(\rho) \]

where \( \ell \) is \( L/L_1 \);
\( \rho \) is \( R/R_1 \); and
\( D_1(\rho) \) is a function which he tabulates.

In the present case, \( \rho = 0.9 \). \( D_1 \) then becomes 0.23 and the expression (18) becomes

\[ 0.427 N_{e0}(t) \]

Now the factor

\[ \frac{e^2}{2 \varepsilon_0 m \omega_0^2} = \frac{1.588 \times 10^9}{\omega_0^2} \text{ cm}^3 \]

So in our situation where \( \omega_0 = (2\pi) \times 9.2 \times 10^9 \text{ Hz} \)

\[ N_{e0}(t) = 540 \Delta f(t) \frac{\text{electrons}}{\text{cm}^3} \]  

(19)

where \( f \) is the ordinary frequency in Hz.

If a uniform distribution is used instead of a diffusion distribution,
\[ N_{e0}(t) = 230 \Delta f(t) \frac{\text{electrons}}{\text{cm}^3} \]  

(20)

For relating electron density change to frequency shift, it is important to notice that the relationship is linear. In our treatment, the constant of proportionality cancels. To know the absolute value of electron number density, it is necessary to know the constant. In this case, we must have some knowledge of the electron distribution in the cavity.

We may combine the results of sections C and D to predict the results of an experiment designed to test spin conservation.

Combining eq. (8) and eq. (19)

\[ \frac{\Delta N_e(t,P)}{N_e(t)} = \frac{\delta(\Delta f)}{(\Delta f)} = \left(1 - \frac{\Gamma_p}{\Gamma_0}\right) K(t) \]

The percent polarization varies from measurement to measurement. Dividing the fractional shift by \([1-\Gamma_p/\Gamma_0]\) places these measurements on the same basis. The resulting unitless "reduced shift" will be expected to lie on \(K(t)\).
III. EXPERIMENTAL APPARATUS AND METHOD

A. Introduction

Having laid some theoretical foundations for the optical pumping process, electron density in the afterglow and its relation to cavity resonance, we must describe the experimental equipment and techniques used in the measurement.

Because the description will naturally separate into distinct topics, it is important first to obtain a picture of the overall arrangement. A microwave cavity is formed around a quartz cell containing gaseous $^3\text{He}$. This cell-cavity is placed in a typical optical pumping arrangement. Waveguide connects the cavity with a source of microwave radiation. A crystal diode which measures the power reflected from the cell-cavity is connected to a rather elaborate detection system which can detect small changes in the resonant frequency of the cell-cavity.
B. Optical Pumping Arrangement

In its essentials, the experimental arrangement used here for achieving optical pumping is the same as those used in several previous experiments in the Atomic Physics Laboratory at Rice University. These are described by Schearer and Byerly. There are some features in which the present set-up differs: the sample cell is cylindrical and made of quartz; the cell is enclosed in a microwave cavity, coupled by an iris to a waveguide; the discharge is pulsed; and the steady magnetic field is in the neighborhood of 200 Gauss.

1. The Sample Cell-Cavity

The sample cell is in the form of a right circular cylinder of fused silica (quartz). Quartz was used instead of pyrex because the former has a lower dielectric constant and thus, will not degrade the cavity Q as much as the pyrex. The cell length was 1.85 inches, the radius, 0.89 inches. A 6 mm OD graded seal (Corning 7900 to 7740) was attached perpendicularly at one edge (see Fig. 2). After elaborate cleaning procedures (similarly to those described by Stockwell, p. 48) the cell was filled with 2 Torr of $^3$He.

This sample cell forms the basis for the microwave cavity. One end of the cavity is silver plated brass in the form of a circular plate with a small lip on its periphery, which enables the cell to be seated firmly. This plate contains the coupling iris and two holes, one of which allows
Fig. 2 The Cell-Cavity.
the graded seal and tip-off to extend outside the cavity while the other permits the light transmitted through the cell to be monitored.

The iris is an elongated hole on a radius of the cavity and extending along the long dimensions of the waveguide. This geometry facilitates excitation of the $TE_{011}$ mode of the cavity. A section of waveguide with a teflon wedge whose position is adjustable is attached to this end of the cavity. The adjustable teflon wedge facilitates variation in the coupling of waveguide to cavity.

The other end of the cavity is constructed of copper screen which transmits 87% of the light incident upon it. This copper mesh was obtained from Buckbee Mears Company, St. Paul, Minn. It is their 30 line Copper #30 rule screen. For stability, the screen is clamped between two rings of brass. This screen ring is attached with rubber bands to the solid brass cavity end, holding the sample cell firmly in place between the two ends.

The body of the cavity is formed by wrapping eight strips of copper, 0.14 inches wide and 0.003 inches thick, around the sample cell. These are spaced uniformly and attached with teflon tape, making sure that no strip touches either cavity end.

This form of cavity is the result of several attempts to strike the best compromise between cavity Q and transmission of the depolarizing radiation through the cavity.
The splitting of the $^3\text{He}$ ground state sublevels in a magnetic field is 3.2 KHz/Gauss. At the value of steady magnetic field used in this experiment (about 227 Gauss), the radio frequency radiation for depolarizing was about 730 KHz. Radiation of this frequency was shielded by both a perforated brass cavity and by the solid Mylar foil wrapping described by Stockwell. The strip approach, however, permitted the transmission of the rf energy, while not causing an extreme degradation in the cavity $Q$, since in the $\text{TE}_{011}$ mode there are no currents flowing parallel to the $z$ axis. The strips are several skin depths at the microwave frequencies used.

2. The Discharge

The discharge in the cell was lit with a small 100 KHz oscillator whose output terminals were connected to the front screen and to the brass cavity seat. This oscillator was pulsed at the rate provided by the time base (see below, p. 46), by connecting the grid of the oscillator tube to a General Radio type 1217-B pulse generator. The fixed bias on the tube was so adjusted that with no pulse the tube would be biased off. Use of the GR 1217-B allowed for a variation in pulse length independent of the pulse rate.

The 1217-B has several pulse outputs; these were used to control various aspects of the discharge. A positive-going pulse during the pulse period was used to drive the
grid of the oscillator, thus turning on the discharge. A negative-going pulse during the pulse period was used to bias off both a diode and a gas thyratron connected across the oscillator output. On termination of the pulse, both thyratron and diode began conducting, helping rapidly to quench the oscillation. The generator provides a positive-going pulse at the end of the pulse period, a "delayed pulse". This was used to start the 50 MHz oscillator described below.

Pulsing the discharge had two significant effects: it became necessary to pump for longer periods to achieve the equilibrium polarization; the polarization was strongly dependent on the duty cycle of the discharge pulsing. The sampling method limits the duty cycle since the sampling must occur twice during each afterglow period. At 90 Hz, the total period is 11.1 milliseconds. It was found that 4 milliseconds was the longest discharge-on time consonant with the sampling technique. Polarizations from 8% to 10% were obtainable with this duty cycle.

The rf which excited the discharge was observed with an oscilloscope. It was found that careful adjustment of thyratron bias and pulse-on time could achieve rf quenching within a cycle after the end of a pulse.

In order to simplify the calculations (p. 16), it was desirable to remove from the afterglow the electrons that had been produced during the discharge itself. The electron density measured after the pulse was then presumed to be due
to production mechanisms in the afterglow. The delayed pulse from the 1217-B triggered a E-H Laboratories Model 131 pulse generator. This generator has a variable delay and a variable pulse width. Its output controlled the output of a 50 MHz oscillator-amplifier which was coupled to the cell-cavity together with the 100 KHz rf which lit the discharge. It was found that a pulse of 50 MHz rf about 150 microseconds in length and coming about 100 microseconds after the 100 KHz oscillator shut-off would sweep the electrons to the walls where they would be lost as free electrons. By monitoring the reflected power (proportional to the electron density) it was possible to adjust the intensity of the 50 MHz rf so that it would not light another discharge, yet would sweep all the electrons from the afterglow.

3. Optical and Mechanical Arrangement

The cell-cavity was placed in the center of a solenoid 18.79 inches long, with end corrections. This solenoid was wound by Byerly and is described in his thesis. He measured the inhomogeneity to be 6 parts in $10^5$. The large solenoid was used to achieve higher polarizations since an experimental result of Hatfield shows a dependence of percent polarization upon magnetic field strength. At a current of about 15 amperes provided by a Harvey-Wells HS 1365-B power supply, the solenoid provided a field of 227 Gauss.
From Hatfield's results, this was a suitable and convenient value for optical pumping in $^3$He at 2 Torr.

The cell was oriented so that its axis was coincident with the axis of the solenoid. This axis was placed along the optical axis of the resonance radiation apparatus which consisted of a $^4$He button lamp, a spherical mirror, condensing lens, and circular polarizer (see Fig. 3).

The lamp was a hollow Vycor button 1 inch in diameter connected to a pyrex reservoir through a graded seal. The reservoir was found necessary to minimize the pressure drop as the helium diffuses through the Vycor. The lamp was filled with about 10 Torr $^4$He. A strong discharge was lit in the lamp by placing it in a two turn center-tapped coil which was in the plate circuit of two 4CX300-A tubes operating in the free running multivibrator mode. Stabilized power supplies furnished plate and screen voltages for the tubes; the plate voltage was 900 volts and the plate current 300 milliamperes. Direct current was used for the filaments to reduce 60 Hz hum in the optical signal. It was necessary to cool both the plates of the 4CX300-A tubes and the Vycor button with compressed air.

The light transmitted through the cell was monitored through the 0.25 inch hole in the center of the rear brass plate. For convenience, a prism mirror was placed against the hole and the light reflected 90° to a PbS photodetector. This detector was enclosed in a brass and copper tube about
Fig. 3. The optical pumping arrangement: cut-away view through solenoid.
1/2 inch in diameter and 1 1/2 inches long and arranged so that the only light entering it was light transmitted through the cell-cavity. The detector was properly biased and the optical signal observed with an oscilloscope.

Depolarizing was effected by placing a small coil (11 turns #22, 1 1/2 inch Lucite form) with its axis perpendicular to the axis of the cell-cavity and exciting this coil with a frequency corresponding to the ground state sublevel separation. For this rf signal, a Hewlett-Packard 606-A signal generator was used. The bandswitch of the signal generator was used to turn this Larmor radiation on and off. It was found that this method eliminated some transients that increased noise in the measurement of shift.
C. Microwave Circuitry

The microwave circuit is shown in the left hand side of Fig. 4. It is straightforward and uses standard X-band components except for the cavity and the section of waveguide which joins it to the system. These have been described above.

The klystron used was a Westinghouse WL 122. It was powered by a Hewlett-Packard 716B power supply. The use of the frequency meter and the cathode ray oscilloscope associated with it will be explained in the following section. The circulator permits incoming power to enter the cell-cavity and reflected power from the cell-cavity to fall on the diode detector. The Hewlett-Packard 382-A attenuator is used together with the Hewlett-Packard 431-B power meter to adjust the power entering the cavity.

Forming the cavity so as to accept optical and low frequency rf radiation and placing a quartz container within tend to lower the Q. With the coupling used in the present experiment, the measured Q was about 700. The probing power of the microwaves was about 150 microwatts. This had no effect on polarization or on electron density.

Operating the cell-cavity in the TE_{011} mode is essential to our calculations. The modes were carefully sorted by Stockwell, who used a solid brass cavity of the same dimensions as the cell-cavity. He introduced the screen and slots separately. A further assurance of certainty is added by the
Fig. 4 Block diagram of microwave circuit and sampling system.
fact that the front and back plates are electrically insulated from the body. All modes except the TE$_{011}$ have current which flows from body to ends. These modes would have extremely low $Q$ in the present cavity and would be essentially suppressed. With no discharge in the cell, cavity resonance occurred at 9227.7 MHz.
D. Sampling and Source Compensation Technique

The shift in resonant frequency of the sample cell-cavity, expected if spin conservation holds, was sought by means of microwave diagnostic techniques developed by Freiberg and Weaver. They developed these methods to measure electron densities as small as \(2 \times 10^4/\text{cm}^3\) in the afterglow of pulsed discharges. Such techniques make it possible to achieve high sensitivity while preserving a usable signal-to-noise ratio by the use of synchronous detection.

1. Method

The shape of the cavity frequency response curve (it is essentially Lorentzian) and the fact that this curve shifts its center frequency with changing electron number density within the sample cell suggests its use as a discriminator. That is, it can be employed as a device which may translate a frequency variation into an amplitude variation. Consider, for example, the microwave probing frequency as fixed, and having a value that falls somewhere within the response curve of the cell-cavity. This response curve actually represents a plot of reflected power versus frequency. So at the given probing frequency there will be a certain value of reflected power received at the detecting crystal shown in Fig. 4. As the number of electrons in the cell-cavity changes, the response curve will move on the frequency scale. If the probing frequency remains fixed, there will be varying values
of reflected power reaching the crystal. Thus, the varying frequency of the cavity has been translated into a varying amplitude of power at the detector.

If the probing frequency remains in a linear portion of the cavity response curve throughout the shift of the cavity, the crystal detector response is a fair representation of the cavity frequency response. The crystal signal can be displayed on a cathode ray oscilloscope synchronized with the frequency of discharge pulsing. The resulting pattern will represent the time varying frequency of the cavity during and after discharge if the probing microwave frequency remains in a linear portion of the response. It should be noted that for a relatively weak discharge in the cell-cavity used in this experiment, it was hard to achieve this condition of linearity. However, the measurement of shift on depolarization represents a very small change of frequency. It was always possible to preserve linearity in this latter case.

The above method of shift observation with an oscilloscope proved to have insufficient sensitivity in the present experiment. Increasing the gain showed only that the signal-to-noise ratio was too high for this approach. A periodic sampling and source compensation technique provided the needed sensitivity while keeping the noise bandwidth low.

Reference to Fig. 5 will help in understanding the
Fig. 5 Periodic sampling and source compensation.
following description of sampling and compensation technique. (a) represents the voltage at the detecting crystal which monitors power reflected from the cell-cavity. It is assumed that we remain in a linear portion of the response, so that the voltage at the crystal represents the frequency of the cavity and thus the density of electrons in the cell. Two periods are represented; it should be noted that the 50 MHz pulse, the "killing" pulse removes electrons from the cell (to the walls where they recombine) at the time of termination of the active discharge. The singlet and triplet metastables are not charged particles and thus will not be swept out of the afterglow. They continue to collide and diffuse; thus, the electron density takes on the shape shown.

Suppose that the crystal voltage at a time \( t_1 \), say \( V_1 \), is stored in some type of device and "remembered". At time \( t_2 \), when the crystal voltage is \( V_2 \), suppose that this new voltage is stored in the device and the memory of the past voltage is destroyed. Suppose further that \( t_1 \) and \( t_2 \) are a half period apart. A time plot of the voltages stored in the device appears in (b). It is simply a square wave of amplitude \( V_1 - V_2 \). If the time \( t_2 \) is adjusted so that \( V_2 \) represents the frequency of the cavity when all the electrons have diffused to the walls, then the amplitude of the square wave is proportional to the voltage (and thus the frequency) at time \( t_1 \).

Since the frequency of the square wave is the same as
that of the discharge, we have the possibility of using synchronous detection, or "lock-in" techniques. This greatly increases the signal-to-noise ratio. Greater gain is possible within the limits of amplifier linearity.

With increasing gain, the voltage $V_1 - V_2$ may become quite large, exceeding the limits of linearity of associated amplifiers. A null technique—source compensation—circumvents this latter difficulty. (c) represents the cavity response at time $t_1$ in the afterglow; cavity response has been represented as the crystal voltage, for convenience. The probing frequency intersects the response at voltage $V_1$. (d) represents the cavity response at $t_2$; for the same probing frequency, the voltage is $V_2$. Suppose, however, that at time $t_2$ the probing frequency were shifted to $f_2$. In this case, the voltage would be $V_1$. So the probing frequency can be made to compensate for the cavity frequency shift. Needless to say, the response in time at the crystal detector would be $V_1 - V_1 = 0$.

This null "signal" can be fed into a lock-in amplifier, referenced to the discharge pulsing frequency and the square wave frequency. The gain can be greatly increased. When the cell-cavity is depolarized, the frequency shift (if any) will not be compensated and can be read as a signal on the lock-in amplifier. In the present experiment, this signal was recorded on a standard strip-chart recorder connected to the lock-in amplifier.
Besides the nulling procedure described above, some care must be taken to insure that a) \( f_1 \) (and thus \( f_2 \)) is in a linear portion of the cavity response curve and b) the klystron gives equal power at \( f_1 \) and \( f_2 \). The method of taking these precautions as well as that of calibrating the shift will be described after the experimental apparatus is introduced and explained.

2. Apparatus

The time reference for the system was provided by a Hewlett-Packard Type 202-A function generator. This generator was operated in the square wave mode at a frequency of 90 Hz. It triggered the GR 1217-B and thus set the rate of the pulsed discharge (see Fig. 4).

The afterglow signal must be sampled twice each cycle (see above, p. 44). The square wave output was fed into a device which provided a trigger pulse at twice the square wave frequency.

These 180 Hz trigger pulses were used to control a Data Pulse 101 pulse generator. This generator has a variable delay and a variable pulse width. Its output was fed to a Redcor 770-708 Sample and Hold device. This Sample and Hold (S&H) device is such that when a voltage greater than 3 volts appeared at its control terminal, the signal at the input would appear at the output terminal. When the control voltage decreased, the output would hold whatever voltage the
input had seen at the instant that the control voltage fell below 3 volts.

The output pulses of the Data Pulse 101 could thus control the S&H device. The S&H would "sample" the input signal during the time of a pulse from the 101 (greater than 3 volts). This sampling time was about 30 microseconds. It would then "hold" this signal voltage until the next pulse from the 101, at which time it would sample and hold the signal, and so one. The variable delay of the Data Pulse 101 made it possible to sample the signal at different times in the afterglow period.

The output of the S&H, consisting of 90 Hz square waves with amplitude proportional to crystal signal at a given time, was fed to the input of a PAR JB-4 Lock-in amplifier. This was referenced to the square wave time base. Its output was connected to a Texas Instruments strip-chart recorder.

The output of the square wave generator was fed through an attenuator to the reflector modulation input of the klystron power supply. The klystron output then alternated between frequencies $f_1$ and $f_2$. The setting of the attenuator controlled the square wave modulating voltage and thus the value of $|f_2 - f_1|$. The attenuator was adjusted so the signal to the Lock-in was nulled out. The gain was increased by using a Philbrick preamplifier with a gain of 50 and the amplifiers internal to the JB-4.
3. Experimental Considerations

The built-in delay of the Data Pulse 101 was used to set the sampling time. The square wave output of the S&H device was observed with an oscilloscope. The control terminal of the S&H was then switched to a steady 3 volts, causing it to sample the entire afterglow pattern. Switching alternately between these two patterns together with the persistence of the trace made it possible to determine the sampling time in relation to the cavity frequency shift.

For certain settings of the sampling time, it was found that the compensating square wave was of the wrong phase. To remedy this, a triggered bistable multivibrator was inserted in the compensating circuit. The output of either of its two transistors could be chosen as the compensating square wave; one or the other would compensate properly since they were 180° out of phase. The necessary 180 Hz trigger to obtain a 90 Hz square wave output was obtained from the frequency doubling circuit (see Fig. 4).

Noise was often a problem. Standard approaches were taken to eliminate ground loops. There was some drift, probably thermal in origin. There was also some random noise in the Lock-in output.

The procedure for taking the measurements was to allow the system to pump for several pumping times, to compensate the S&H output, increase the gain of the JB-4 Lock-in, and then to depolarize by switching on the resonance radiation.
The bandswitch of the 606-A signal generator was used for this switching, since other switching arrangements introduced undesirable transients on the signal. The resulting shift was then recorded on the strip-chart recorder. The absorption in the polarized and depolarized states was measured optically. This measurement was often made simultaneously with the frequency shift measurement.

4. Calibration

In order for the shift in Lock-in output to be interpreted as a frequency shift it was necessary to take some measures regarding linearity and to find certain calibration factors.

It is necessary that the klystron yield the same power at both $f_1$ and $f_2$. Otherwise, equal detector voltages at $f_1$ and $f_2$ will not represent frequency compensation and a shift of the Lock-in output will be ambiguous. This equal power condition was met by observing the klystron output with the oscilloscope (see Fig. 4). The reflector voltage level and mechanical adjustment were set so that the signal was compensated at the same time that $f_1$ and $f_2$ gave equal detector output.

It is also important that the probing frequency fall in a linear region of the cell-cavity response curve. A plot of reflected power of the cell-cavity versus frequency was made for the case of no discharge. The frequency $f_1$ or $f_2$
which corresponded to the no-discharge, zero electron density was set to a linear portion of the curve. It was frequently found necessary to repeat the procedure of the preceding paragraph at this point.

For calibration, it is necessary to know two relations: the change in klystron frequency with applied reflector modulating voltage \( \frac{\Delta f}{\Delta V} \), and the change in Lock-in output with reflector modulating voltage, \( \frac{dV}{dI} \). The output of the recorder and that of the Lock-in were calibrated together. To obtain \( \frac{\Delta f}{\Delta V} \), the output of a crystal detector following the calibrated wavemeter was monitored (see Fig. 4). When the klystron frequency was modulated with the square wave, there were two "dips" observed in the crystal output, at \( f_1 \) and \( f_2 \). These were read on the wavemeter and, for more accurate determination, the klystron was stabilized on each dip and the frequency read with a frequency counter. The modulating square wave voltage was read on a calibrated Hewlett-Packard Type 545 oscilloscope.

To obtain \( \frac{dV}{dI} \), the distance the recorder pen moved was noted for a small change in the reflector modulating voltage. Because of the sensitivity of the system, it was necessary to use the calibrated attenuator on the Lock-in amplifier. With these conversion factors, the recorder output could be interpreted as a frequency shift.
IV. EXPERIMENTAL RESULTS

The procedure explained in Section D, Parts 3 and 4 was followed for several times in the afterglow. A typical signal is shown in Fig. 6. The rf was switched after the shift to insure that transients were not responsible for the signal.

Using the measured value of polarization, the reduced shift was calculated and plotted in Fig. 7. The plot of $K(t)$ indicated the theoretical value of reduced shift and is included for comparison.

There is useful auxiliary information contained in some of the measurements made in performing the experiment. Percent absorption of 1.08 micron radiation was measured simultaneously with frequency shift. Using eq. (20), this yields a plot of percent absorption (proportion to metastable density) versus electron density, Fig. 8.
Fig. 6 A typical shift signal: the Lock-in output on depolarizing.
Fig. 7 Values of reduced shift (measured frequency shift divided by $1 - \frac{\Gamma_p}{\Gamma_0}$) compared with $K(t)$ in the helium afterglow.
Fig. 8 Absorption of 1.08 micron light versus electron density and frequency shift of the cell-cavity.
V. SUMMARY AND CONCLUSIONS

We have demonstrated that electron spin is conserved in the collision of two helium triplet metastable atoms. The amount of variation in the experimental data prevents our making statements regarding the exact extent of this conservation law, but the observed shift has been compared to a theoretical prediction of frequency shift relating to spin conservation.

Much of the variation in the data may be due to the presence of noise on the signal and to the fact that there is some uncertainty (± 15%) in determining the value of polarization used in calculating reduced shift.

Several extensions and improvements of the measurements presented here suggest themselves.

One of the weaknesses of the theoretical treatment of density of electrons in the afterglow was the reliance on some rather arbitrary assumptions regarding the relative populations of singlet and triplet metastable atoms and their cross sections in collision. It might be possible to circumvent this weakness by some method that would destroy the singlet metastables by exciting them to higher state from which they could radiate. Another approach would be to determine somehow the ratio of singlets to triplets at different times in the afterglow. This could then be correlated with measurements of the frequency shift at
different afterglow times.

A measurement of the spin conservation shift in $^4$He would be valuable in related optical pumping experiments. It is of some interest to examine the shift in steady discharge for several values of cell pressure.

Finally, the technique of measuring electron density in optical pumping cells can be applied to other optical pumping experiments. In some of these, it is desirable to know simultaneously the electron density and the other customary optical pumping parameters.
VI. REFERENCES

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VII. ACKNOWLEDGEMENTS

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