QUADRUPOLE TRANSIENT EFFECTS
AND
A SUPER-REGENERATIVE SPECTROMETER
by
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A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
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in the Department
of
PHYSICS

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Department of PHYSICS

The University of British Columbia,
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Date 12 September 1963
A field modulated super-regenerative spectrometer was constructed. The theory of its operation was developed and put to test by observing the pure quadrupole resonance of Chlorine 35 in Para-di-chlorobenzene powder at room temperature. The spectrometer's operation is closely related to the quadrupole transient effects. So another experiment was done to measure the amplitude and the decay time constant of Free Induction Signal in Para-di-chlorobenzene as a function of pulse width and magnetic field, using a pulsed r.f. transmitter, constructed for this purpose. The results of this experiment were then applied to the theory of the spectrometer to explain its behaviour.
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I. INTRODUCTION

The purpose of this work is to study the operation of a super-regenerative spectrometer by observing the pure quadrupole resonance of Chlorine 35 in para-di-chlorobenzene in powder form.

A high inherent gain (of the order of $10^6$) and the ease with which frequency can be swept over a wide range make the superregenerative spectrometer very useful in searching for unknown quadrupole resonance lines. The oscillator used in the spectrometer is usually of the Colpitt's type. However, it differs from the standard form because it is turned off and on at a certain rate by applying a suitable "quenching" voltage at one of the electrodes of the oscillator tube or the oscillator may be made self quenching by connecting an RC network of sufficiently large time constant to the grid of the tube. Thus the output of the oscillator consists of a series of pulses, the frequency of which is the same as that of the quench voltage. The width of the pulse, i.e. the duration of the on-time of the oscillator can be changed by suitable controls.

The oscillator, in quadrupole resonance work, is usually operated in the logarithmic mode i.e. the r.f. oscillations reach a steady value before they are quenched. In the absence of any signal the r.f. oscillations are initiated by noise. The time during which the r.f. oscillations attain their steady value depends upon the amplitude of the initiating signal. When the oscillator's frequency is swept through resonance, a nuclear signal is induced across the coil. Now the r.f. oscillations start from the signal plus noise, so they attain their steady
value sooner which increases the pulse area. In the super-regenerative spectrometer the oscillator is followed by a detector and an integrator. Thus the integrated output of the detector increases as the frequency of the oscillator passes through resonance, thus giving an indication of resonance.

The frequency spectrum of the oscillator, because of quenching, consists of a main central frequency with side bands on either sides separated by the quench frequency. If the side bands are of sufficient intensity, they can also excite the resonance as the oscillator's frequency is scanned. Thus the output of the spectrometer does not consist of a single line but a number of lines. This property of the super-regenerative method is especially confusing when it is necessary to detect small splittings of the quadrupole resonance.

The generation of the nuclear signal by the oscillator at the resonance frequency is closely associated with the quadrupole transient effects (1) which can be qualitatively described as follows.

The quadrupole system has no net magnetization because of the two fold degeneracy of the pure quadrupole levels. However, there exists a magnetization $\vec{M}_0$ parallel to the symmetry axis of $\nabla E$ due to the difference in population between the $|m\rangle$ and $|m-1\rangle$ states and similarly an equal and opposite magnetisation exists because of $-|m\rangle$ and $-|m-1\rangle$ states. The discussion here is only confined to $I = \frac{3}{2}$ and a quadrupole system with axial symmetry, so that the eigenfunctions of $I_z$ given by $I_z|m\rangle = m|m\rangle$ with $m = \pm \frac{1}{2}, \pm \frac{3}{2}$
are also the eigen functions of the pure quadrupole Hamiltonian. The linearly polarized r.f. magnetic field applied during the pulse is equivalent to two circularly polarized fields, the one in phase with the precessing magnetization vector rotates it by angle $\alpha$. The remaining component of the linearly polarized r.f. magnetic field rotates the other magnetization vector by the same angle $\alpha$. Thus both rotating components of r.f. field are utilized in quadrupole resonance. After the pulse, each of the magnetization vectors begins to precess about the symmetry axis at an angle $\alpha$, in opposite directions and thereby they give rise to an oscillating magnetization parallel to the axis of the r.f. coil. The voltage induced across the r.f. coil because of this oscillating magnetization forms the induction signal. Thus in quadrupole pulse experiments the transmitting and receiving coils are essentially the same. The induction signal begins to decay with a time constant $T_2$ because of spread in precessional frequency of the nuclei.

In order to observe the quadrupole resonance signals, the super-regenerative spectrometer is usually operated such that the time between two successive pulses is much shorter than $T_2$ (about $\frac{1}{10}$ of $T_2$), so the induction signal following a pulse is only partially decayed during the off-time. The voltage across the coil at the end of the off period is responsible for the initiation of the next burst of r.f. oscillation and it is this voltage that determines the spectrometers action. The actual signal obtained by the spectrometer is observed by subjecting the r.f. coil containing the specimen to a sinusoidal magnetic field. The magnetic field drastically changes $T_2$ and
thereby causes smearing of the resonance line twice a cycle. Thus the signal is modulated at twice the frequency of the magnetic modulation. Thus the modulation allows the use of a narrow band-width amplifier which improves the signal to noise considerably. The noise is further reduced by the use of a phase sensitive detector. Thus we can study the theory of the spectrometer's operation only when the value of $T_2$ as a function of the various parameter of the spectrometer is known.

The first part of the thesis describes the pulse experiment which was done to measure the amplitude and the decay time constant of the induction signal as a function of the magnetic field and pulse width with a discussion of the results obtained. The theory of the spectrometer is developed in part II and then the results of part I are used to interpret the theory.
II. THEORY

The Pure Quadrupole Induction Signal.

As discussed in the article by Cohen and Reif (2) the Hamiltonian for the interaction of the quadrupole moment of a nucleus with an axially symmetric electric field gradient \( \nabla E \) at the nuclear site due to surrounding changes is given by:

\[
\mathcal{H}_q = \frac{e Q \epsilon}{4 I(2I-1)} \left[ 3I_z^2 - I^2 \right] \tag{2.1}
\]

where \( \nabla E \) is symmetric about an axis in space, say Z-axis.
\( e \) \( \epsilon \) is the scaler electric field gradient.
\( e Q \) is the scaler nuclear electric quadrupole moment.

As \([\mathcal{H}_q, I_z] = 0\), the eigenfunctions of the quadrupole interaction \( (\psi_m) \) are simultaneous eigenfunctions of \( I_z \).

Therefore

\[
\mathcal{H}_q \psi_m = \frac{e^2 \epsilon Q}{4 I(2I-1)} \left[ 3m^2 - I(I+1) \right] \psi_m = E_m \psi_m \tag{2.2}
\]

and \( I_z \psi_m = m \psi_m \).

An r.f. field \( 2\hbar \cos \omega t \) which couples to the nuclear magnetic moment induces transitions between the various energy levels given by (2.2) corresponding to \( \Delta m = \pm 1 \). Because of the degeneracy of the \( \pm m \) states, there are \( I \) transition frequencies for integral spins and \( I = \frac{1}{2} \) for half integral spins. Being concerned with Chlorine, we will consider a single transition for \( I = \frac{3}{2} \) to illustrate the general properties of in-
duction signals.

In nuclear magnetic resonance experiments (3), there exists initially a net magnetization \( \vec{M}_0 \) in the direction of the static magnetic field \( H_0 \) (Z direction) because the nuclear spins when in thermal equilibrium with their surrounding are populated among the \((2I + 1)\) levels according to the Boltzmann distribution law. This magnetization is rotated by an r.f. magnetic field \( 2H_1 \cos \omega_0 t \) applied at right to \( H_0 \) by an angle \( \gamma H_1 t \) provided \( \frac{1}{t} \omega \gg \Delta H \) where \( \omega \) is the width of the applied r.f. pulse, \( \gamma \) the gyromagnetic ratio of the nucleus, \( \omega_0 = \gamma H_0 \) the resonance frequency and \( \Delta H \) denotes the line width. After the pulse non-vanishing \( x - y \) components of \( \vec{M} \) exist and a voltage proportional to \( M_0 \sin(\gamma H_1 t \omega) \) is developed across the sample coil placed at right angles to \( H_0 \). The signal decays in a time \( T^* \), the time taken for the nuclear spins to "dephase".

In case of quadrupole systems, it can be shown that the expectation value of nuclear magnetization is zero, at thermal equilibrium.

Expanding in terms of the eigenfunctions of the quadrupole interaction

\[
\psi = \sum_m C_m \psi_m
\]

\[
\hat{I}_z = \langle \psi^* | I_z | \psi \rangle = \sum_m m C_m^* C_m = \sum_m N_m
\]

At thermal equilibrium, the population of the states is governed by the Boltzmann equation.
\[ N_m \alpha e^{-\frac{E_m}{KT}} \]

But \( E_m = E_{-m} \)

\[ \therefore N_m = N_{-m} \]

so that \( \bar{I}_z = 0. \)

Thus no macroscopic nuclear magnetization is present at thermal equilibrium. It is therefore not obvious that free induction effects similarly to those previously mentioned can be produced there. However, a quantum mechanical calculation (4) shows that the effect of inducing magnetic transitions by pulses of the r.f. magnetic field is to produce a macroscopic oscillating nuclear magnetization. For the case of a symmetric electric field gradient \( \nabla E \), this magnetization is produced in the plane perpendicular to the axis of symmetry of \( \nabla E \), and it precessional motion can be given a semiclassical description.

A quadrupole system has no net macroscopic magnetization due to two fold degeneracy of \( \pm m \) states. However, there exists a magnetization \( \vec{M}_0 \) along the symmetry axis due to difference in population between \( |m\rangle \) and \( |m-1\rangle \) states and an equal and opposite magnetization due to \( -|m\rangle \), \(-|m-1\rangle\) states. We will consider these two magnetization vectors separately.

The population difference between \( |m\rangle \) and \( |m-1\rangle \) states, at thermal equilibrium and for \( E_m - E_{m-1} / KT << 1 \), is given by Boltzmann statistics as \( N(E_m - E_{m-1}) / KT(2I+1) \) where \( N \) is the no. of resonant nuclei. Therefore the magnetization \( \vec{M}_0 \) due to this difference of population is

\[ M_0 = N\hbar \frac{(E_m - E_{m-1})}{KT(2I+1)} \quad (2.3) \]
The linearly polarized r.f. magnetic field $2H_1 \cos \omega t$ applied at right angles to symmetry axis (Z axis) is equivalent to two fields rotating in x y plane, one in clockwise sense and the other in counter-clock-wise sense. The counter-clockwise rotating magnetic field rotates the magnetization $M_x$ by an angle $\sqrt{3\gamma H_1 \omega t}$ and then there exists a magnetization along each of the three axes. During the pulse the components of magnetization $M_x$, $M_y$ and $M_z$ obey equations similar to Bloch's equation (5). A transformation is made to a frame of reference in which the (x, y) plane rotates at the frequency of the applied r.f. field $H_1$. Therefore the vector $(M_x, M_y, M_z)$ in the laboratory frame transforms to the vector $M(u, v, M_z)$ in the rotating frame, where $H_1$ is fixed parallel to the $u$ component. The transformation is given by (for positive $e^2 q Q$)

\begin{align*}
M_x &= u \cos \omega t - v \sin \omega t \\
M_y &= -(u \sin \omega t + v \cos \omega t) \quad (2.4) \\
M_z &= M_z
\end{align*}

Similarly the magnetization due to $-m, -(m - 1)$ states is rotated by the clockwise rotating magnetic field. Thus both the rotating components of the r.f. field are utilized in quadrupole resonance. $M_x, M_y$ for this case are given by

\begin{align*}
M_x &= u \cos \omega t - v \sin \omega t \\
M_y &= +(u \sin \omega t + v \cos \omega t) \quad (2.5)
\end{align*}

The observed induction due to equal contribution from both pair of $m$ states is obtained by (2.4) and (2.5).

\begin{align*}
M_x &= M_x(m) + M_x(-m) = 2(u \cos \omega t - v \sin \omega t) \\
M_y &= M_y(m) + M_y(-m) = 0 \\
M_z &= M_z(m) - M_z(-m) = 0.
\end{align*}
FIG. 2.1
Thus no signal of induction would be detected in a coil oriented at right angles to the r.f. coil which serves both to detect $M_x$ as well as transmit $2H_1$.

Fig. (2.1) shows a vector model of macroscopic spin precession in an axial electric field gradient for positive signs of $e^2qQ$ and $\gamma$. The special case is shown where the macroscopic moment $M(m)$ and $M(-m)$ are rotated by $90^\circ$ about the r.f. field $H_1$ during a pulse.

If a small magnetic field $H_0$ is applied to the spins along Z axis for example, such that $\gamma \parallel H_0 < e^2qQ$ the entire vector diagram can be thought of as precessing about $H_0$ in a direction determined by the sign of $\gamma$. Therefore the symmetry of alignment about the X axis of $M(m)$ and $M(-m)$ is removed, which in essence means that the degeneracy of the $\pm m$ states is removed. A low frequency modulated induction signal will then appear along the y axis as well as the x axis due to the additional precession imposed by $H_0$. 
III. APPARATUS AND EXPERIMENTAL PROCEDURE

A. Description of the Apparatus.

A block diagram of the apparatus used for the pulse experiment is shown in Figure (3.1).

The block and circuit diagram of the pulsed transmitter are given in Figures (3.2) and (3.3) respectively. The first part of tube $V_1$ converts the positive pulses from Tektronix Type 163 Pulse generator into negative pulses. The screen grid, grid and cathode of tube $V_3$ together with the tuned circuit are connected as a Hartley oscillator which is allowed to oscillate only when the tube $V_2$ is switched off by the negative pulse at its grid. Thus $V_2$ acts as a gate. The special feature of the transmitter is that the oscillator is electron coupled to the plate of $V_3$ and thus to the load which makes it quite immune to the changes of the load. $V_4$ acts as a tuned buffer amplifier whose output is fed to a tuned push-pull power amplifier ($V_6$) through the gate formed by $V_5$. The power amplifier $V_6$ operates only when the negative pulse from $V_1$ switches the gate tube $V_5$ off, which allows the use of the 829B tube at much higher voltages than its normal ratings. The cathode of $V_5$ is at -300 volts so that its heater must also be at -300 volts d.c. The 4 μf condenser connected at the output stage is to store the pulse energy. The coils of the Hartley oscillator, tuned buffer amplifier and that of the power amplifier are mounted mutually at right angles to avoid any direct pick-up.
TEKTRONIX TYPE 163 PULSE GENERATOR

PULSE TIMER

C R 0

RC FILTER

DETECTOR

ARENBERG WIDE-BAND AMPLIFIER

FIG31 BLOCK DIAGRAM OF THE PULSE APPARATUS
FIG. 3-2  BLOCK DIAGRAM OF PULSED TRANSMITTER
FIG 33 TRANSMITTER
FIG 3.4 PULSE TIMING CIRCUIT
The circuit of the pulse-timer is given in Fig. (3.4). It consists of four multi-vibrators. The first one is free-running and its R-C time constant determines the repetition rate. It triggers the second multi-vibrator. The R-C time constant of this multi-vibrator determines the delay time. The pulses from the second multi-vibrator trigger the third and fourth multivibrators. The two 6SL7 tubes mix the pulses producing a trigger for the transmitter.

B. Measurement of $T_2$.

The transmitter was mounted just at the top of Helmholtz coils used to provide a d.c. magnetic field. The coil containing the sample i.e. para-di-chlorobenzene was suspended at the centre of the Helmholtz coils by stainless steel tubing about 10" long. This was done to avoid the use of a half wave-line. The Chlorine 35 pure quadrupole resonance in p-dichlorobenzene was found to be at 34.2 MC/sec at room temperature and 34.7 MC/sec at liquid nitrogen temperature as measured by a super-regenerative spectrometer. These results were in agreement with the previous measurements as given in (6) and (7). The preamplifier was tuned to 34.2 MC/sec by observing proton induction signals in glycerine. The various stages of the transmitter were tuned to 34.2 MC/sec by a Halicrafter's receiver model SX-42. The pure quadrupole induction signal was seen without much difficulty. The signals under the various conditions of magnetic field and pulse-width were recorded on film with a Dumont scope camera type 2620.
The line shape of the induction signals can be approximated by a Gaussian function. Thus the amplitude of the induction tail at instant "t" after the pulse is given by

\[ A_t = A_0 e^{-\frac{t^2}{2T_2^2}} \]  

(3.1)

Fig.(3.5) gives two typical decay curves (plot of log A(t) versus \( t^2 \)). The curve A corresponds to zero field and B corresponds to a magnetic field due to 75 milliamperes current.

\( T_2 \) measurements were made as a function of magnetic field and pulse width both at room and liquid nitrogen temperatures. The results are given in the next chapter.

C. Measurement of \( T_1 \).

The presence of free induction signals in nuclear quadrupole resonance requires that, before application of the first pulse of r.f., there be a difference in the populations of the energy levels between which transitions are induced. The initial amplitude of the induction signal is proportional to this difference in population, \( n \).

For a spin \( 3/2 \) system,

\[ n = n_{3/2} - n_{1/2} \]

where \( n_{3/2} = n_{+3/2} + n_{-3/2} \) = the population of the \( m = \left| \frac{3}{2} \right| \) states

and \( n_{1/2} = n_{+1/2} + n_{-1/2} \) = the population of the \( m = \left| \frac{1}{2} \right| \) states.

We assume that this difference of population has been established by the nuclei coming into thermal equilibrium with their sur-
roundings before the first pulse has been applied.

Now the effect of inducing transitions is to change the surplus population from its equilibrium value. For a two energy level system the surplus population, when the system is not at thermal equilibrium, will recover toward its equilibrium value exponentially with a time constant $T_1$, the spin lattice relaxation time

$$\frac{dn(t)}{dt} = \frac{n_0 - n(t)}{T_1}$$

where $n_0$ is the surplus population when the spin is at thermal equilibrium and $n(t)$ is the surplus population at a time "t".

Therefore $n(t) = n_0 - \left[ n_0 - n(t_1) \right] e^{-\frac{t-t_1}{T_1}}$.

Suppose we apply pulses of r-f at $t=0$ and at $t=\tau$ , the length of the pulses being $t_w$. $V(t_\omega)$ and $V(\tau + t_\omega)$ are the amplitude of the signal following the two pulses. If, $H_1$ makes an angle $\Theta_1$ with the symmetry axis of $\nabla E$, the following can be shown (8)

$$V(t_\omega) - V(\tau + t_\omega) \propto f(\Theta_1) e^{-\frac{\tau}{T_1}}$$

where

$$f(\Theta) = \sin \Theta \left( \sqrt{3} \gamma H \tau t_w \sin \Theta_1 \right) \left[ 1 - \cos \left( \sqrt{3} \gamma H \tau t_w \sin \Theta_1 \right) \right]$$

Thus even in case of crystalline powder where an integration must be performed over $\Theta_1$, $\frac{1}{T_1}$ is given by the slope of $\log \left[ V(t_\omega) - V(\tau + t_\omega) \right]$ vs $\tau$ curve. At room temperature, $T_1$ was measured by exciting the sample by two pulses of identical widths such that the signal following the first pulse is maximum. For this pulse width the signal following the second pulse was found to be close to its minimum value, though
not quite zero. The amplitude of the signal following the second pulse was measured as a function of the time interval between the two pulses. The value of $T_1$ thus obtained is $26.6 \pm 2.5$ milliseconds.

At liquid nitrogen temperature $T_1$ was expected to be quite long so the sample was saturated at time $t=0$ by a train of closely spaced r.f. pulses which produce the initial non-equilibrium condition of zero population difference. Then at a definite time "t" latter a single pulse was applied to measure the surplus of the population recovered in time "t". The value of $T_1$ thus obtained is $570 \pm 25$ milli-seconds. These values are close to those given in references (9) and (10). A plot of the signal (at liquid nitrogen temperature) versus time is shown in Fig. (3.6).
IV. THE RESULTS OF THE PULSE EXPERIMENT

In a super-regenerative spectrometer, the quadrupole system is excited by a series of r.f. pulses and the signal is observed by applying a sinusoidal magnetic field modulation. The theory of the spectrometer, as discussed in the next chapter, requires a knowledge of $T_2$ and the amplitude of the induction signal as a function of magnetic field and pulse width and also the value of $T_1$, for para-di-chlorobenzene, the substance used to test the super-regenerative spectrometer. The object of the pulse experiment reported here is to provide this information so that the theory of the spectrometer may be worked out.

A. Amplitude and Time Constant of the Free Induction Decay

Fig. (4.1) shows $T_2^*$, the decay time constant of the free induction signal as defined by equation (3.1), as a function of the current through the Helmholtz coils producing the magnetic field for a pulse width of 60 $\mu$sec. The value of the magnetic field in gauss can be obtained by multiplying the current in milli-amperes by .068, as calculated by the dimensions of the Helmholtz coils given in Chapter VI.

By the Figure (4.2) which shows a plot of $\frac{1}{T_2^*}$ against the square of the magnetic field, it is seen that $T_2^*$ is fitted quite well by

$$\frac{1}{T_2^*} = A + K\gamma^2 H^2 \quad (4.1)$$

where $T_2$ is the value of the decay time constant of the free
FIG 4.1 $T_2^*$ vs. H
induction signal in zero field and $T_2^*$ is the value corresponding to field "H". $K$ and $A$ are constants. A discussion, of the constants and the equation (4.1) is given latter.

Fig. (4.3) shows $T_2$ as a function of pulse width in the absence of magnetic field. The general trend is that $T_2$ increases with increasing pulse width. It should be emphasized that $T_2$ is here the decay time parameter for a Gaussian plot of the induction signal versus time as given by equation (3.1).

From figure (3.5A) which shows a representative induction decay it is seen that the decay is only Gaussian for long times. A large fraction (of the order of $\frac{1}{3}$) of the signal decays in a much shorter time than $T_2$. It was difficult to make accurate quantitative measurements of the behaviour of the short time component as a function of pulse width because of signal to noise problems at short pulse lengths and receiver saturation effects. In large magnetic fields ($H \gg 10$ gauss) the induction decay fitted a Gaussian curve over the entire range within the experimental error.

Fig. (4.4) shows the amplitude of the induction signal immediately following the pulse as a function of the pulse-width for the various values of the current producing the magnetic field. The signal seems to reach a broad maxima for pulse widths near 50 $\mu$sec. for low applied fields and at lower pulse widths as the external field is increased.

Fig. (4.5) shows the induction signal as a function of the current (producing the external magnetic field) for the various values of pulse widths. The curves corresponding to 50 and 60 $\mu$ seconds are approximately the same as that of 40 $\mu$ seconds.
FIG. 4.3  $T_2$ Vs. PULSE-WIDTH
(FIELD) MILLI AMP

0

75

100

200

250

300

SIGNAL

PULSE-WIDTH

FIG 4.4  SIGNAL VS. PULSE-WIDTH
FIG 4.5  SIGNAL VS. MAGNETIC FIELD

40\*SEC PULSE-WIDTH

MILLI AMP
pulse width. The curves may be summarized qualitatively by noting that the signal tends to decrease as the applied field is increased, the rate of decrease being greater for longer pulse widths.

B. Discussion of the Observed Characteristics of Free Induction Signal

As shown in Chapter II, the eigenfunctions of pure quadrupole Hamiltonian, in case of axial symmetry are the eigenfunctions of \( I_Z \) (the Z component of the spin).

\[
I_Z \left| m \right> = m \left| m \right> \quad \text{where} \quad m = \pm \frac{1}{2}, \pm \frac{3}{2} \quad \text{for} \quad I = \frac{3}{2},
\]

and the states \( \left| \pm \frac{3}{2} \right> \), \( \left| \pm \frac{1}{2} \right> \) are two fold degenerate. When we apply a constant magnetic field \( H \) at polar angles \((\Theta, \Phi)\) in a coordinate system having the symmetry axis of \( \nabla E \) as Z axis, using first order perturbation theory it can be shown that the effect of magnetic field for \( e^2 Q Q > \gamma H \) is to remove the degeneracy of \( \pm m \) states and also to mix \( \pm \frac{1}{2} \) states and yet leave all other \( m \) states pure (5). The coefficient determining the proportion of \( \pm \frac{1}{2} \) states in the mixed state are functions of \( f(\Theta) = (1 + \tan^2 \Theta)^{1/2} \). Now the time dependent density matrix \( \rho \) can be calculated using the equation of motion

\[
\frac{\hbar}{i} \frac{d\rho}{dt} = - \left[ \mathcal{H}, \rho \right]
\]

where \( \mathcal{H} \) is the total Hamiltonian consisting of the pure quadrupole and the Zeeman parts. The induction signal is the time derivative of \( M_x(t) = \gamma \hbar \text{Trace} (I_x \rho) \). As the sample used was in powder form, the signal obtained by taking the time derivative of \( M_x(t) \) will have to be averaged over all the
values of $\theta, \phi$. The matrix elements of the density matrix contain complicated functions of $f(\theta)$, due to which this averaging becomes very difficult. As this pulse experiment was performed only to know the values of the various parameters occurring in the theory of the super-regenerative spectrometer, it was not considered worthwhile to carry out the averaging due to its very complicated nature.

Instead the results obtained from the pulse experiment have been interpreted semi-empirically based on a physical interpretation of the exact programme described above.

The decrease in the value of $T_2^*$ with the magnetic field can be explained in terms of line broadening because of the Zeeman splitting of the pure quadrupole levels (11). For $e q^2 Q \gg \gamma H$, the frequency corresponding to $|\pm 3/2\rangle \rightarrow |\pm 1/2\rangle$ transition splits into four frequencies; the amount of splitting being dependent upon the applied field $H$ and $\Theta$ (the angle between $H$ and symmetry axis of $\nabla E$). Both $\Theta$ and $H$, being not the same for all nuclei, will give rise to a distribution of the resonance frequency thus broadening the line width and so $T_2^*$ being inversely proportional to line width will decrease.

In the absence of the external magnetic field, the decay of the induction signal being Gaussian, the amplitude of the signal at instant "t" after the pulse is $A(t) \propto e^{-t^2/2T_2^2}$. When the external magnetic field is applied, the signal is further attenuated because of the line broadening which is of the order of $\gamma H$ for large $H$ ($\gtrsim 10$ gauss). As the decay of the signal, in the presence of the applied field, is also found experimentally to be Gaussian, it is reasonable to write
\[ A_t \propto e^{-\frac{T_2^2}{\gamma^2 H^2}} \times e^{-\frac{t}{2}} = e^{-\frac{T_2^2}{\gamma^2 H^2}} \]

\[ \cdot \cdot \cdot \frac{1}{T_2^*} = B + K \gamma^2 H^2 \quad \text{where} \quad B = \frac{1}{T_2^*} \quad (4.2) \]

This relation is the same as equation (4.1) which gives the observed dependence of \( T_2^* \) upon \( H \) with the exception of constant \( B \).

For large \( H \), the major attenuation of the induction signal will be due to line broadening caused by \( H \). So \( T_2^* \) will be of the order of \( \frac{1}{\gamma H} \), and then \( K \) should be of the order of one. The experimental value of \( K \) as obtained by the slope of the curve shown in Fig. (4.2) is 1.7. This provides a fairly good test of the validity of (4.1). The intercept of this curve should be of the order of \( \frac{1}{T_2^*} \) as predicted by the equation (4.2). However this intercept is found to be negative. This is because the values of \( T_2^* \) as shown in Fig. (4.1) are only \( \pm 5\% \) which gives quite a wide range for the values of \( \frac{1}{T_2^*} \) especially at high field. Thus a line can be drawn from the high field points, omitting the low field points, with a positive intercept. But we are concerned with low values of field in the spectrometer, so the curve in Fig. (4.2) has been drawn to include the low field points, even though it has a negative intercept. This means that the constant \( B \) in equation (4.2) has been changed with another constant \( A \) in the empirical equation (4.1) which takes care of the consequences arising due to the departure from the high field approximation.
The decrease of the induction signal with the magnetic field can also be explained in terms of the line broadening. In the limiting case when $H \gg H_1$ ($H_1$ is half the amplitude of the r.f. magnetic field), only those nuclei within a frequency range $\Delta \omega \leq \gamma H_1$ of the frequency $\omega$ of the r.f. field, will be excited so as to contribute appreciably to $M_x$ and $M_y$. The effective value of $M_0$ in equation (2.3) should, therefore, begin to decrease when $H$ becomes of order of $H_1$. Therefore the signal, being proportional to $M_0$, also decreases.

Another factor which also contributes to the attenuation of the signal is the relaxation during the pulse which occurs when $T_2^*$ drops to such a value, due to increase of $H$, that it becomes comparable and finally even much less than $t_\omega$, the pulse width. For small pulse-widths of the order of 10 - 20 $\mu$sec, the angle through which $M_0$ is rotated during the pulse is very small, so the effect of decrease in the effective value of $M_0$ becomes less pronounced and also $T_2^*$ requires a large field ($\approx 20$ gauss) to become comparable with $t_\omega$. This makes the amplitude of the signal more or less independent of the field at short pulse widths, till $H$ get as large as 25 gauss when the relaxation during the pulse becomes significant. This effect is demonstrated by the curves of Fig. (4.5). As in the super-regenerative spectrometer, pulse-widths are of the order of 15 $\mu$sec and the peak value of modulation field is about 3 gauss, we may omit the effect of the modulation field on the amplitude of the signal just following a pulse.

The increase of the signal's amplitude with increasing pulse width for constant $H_1$ can be explained by the fact (12) that the
signal is proportional to \( \sin (\sqrt{3} \gamma H_1 t \omega \sin \Theta_1) \) where \( \Theta_1 \) is the angle between \( H_1 \) and the symmetry axis of \( \nabla E \).

As \( \Theta_1 \) has got a random orientation, so \( H_1 \) is quite inhomogeneous which explains the fact that the maxima observed in the curves of Fig. (4.4) are very broad.
V. THE THEORY OF SUPER-REGENERATIVE SPECTROMETER

A super-regenerative receiver is characterized by the repeated build-up and decay of self-oscillations in a valve oscillator, known as the super-regenerative oscillator, operating on, or near, the signal frequency. The circuit is made alternately oscillatory and non-oscillatory by the application of a periodic voltage to one of the electrodes of the oscillator valve. The source of this periodic voltage is usually a separate quench oscillator, although self-quenching may be arranged by a suitable choice of the grid leak and grid condenser of the super-regenerative oscillator. In either case the quench frequency is necessarily much lower than the natural frequency of the super-regenerative oscillator but must be higher than that of the signal modulation.

The sample is subjected to bursts of high r.f. power by placing it into the oscillator's coil. At resonance the oscillations build up from the nuclear signal voltage developed across the coil, otherwise they start from noise existing in the circuit. During the period of build-up the oscillations may become as much as a million times greater the signal.

There are two clearly defined modes of the operation of the oscillator with separate quench, according to whether or not the oscillations are allowed to build up to an equilibrium value, as in a normal oscillator, before they are quenched. If the oscillations which build up during a single quench cycle are
quenched before they reach the limiting equilibrium amplitude determined by the tube characteristic, their peak amplitude is proportional to the signal (or noise) voltage from which the oscillations grew. The oscillator is then said to operate in the linear mode. If, however, the build-up period is made long enough, the oscillations reach a steady value before they are quenched and the oscillator is said to operate in logarithmic mode, as the output, in this mode of operation, increases as $\log_e(V_2/V_1)$ as signal voltage increases from $V_1$ to $V_2$.

The oscillator was operated in logarithmic mode by a nearly rectangular quench voltage. The oscillator's action under these conditions has been shown in Fig. (5.1). During the quiescent part of the quench cycle, when the valve is not conducting, the total effective conductance is determined by circuit losses, i.e. $G = G_0$ and the voltage across the circuit is that due to noise or nuclear signal. As soon as the quench voltage gets higher than the voltage at which the oscillations start, the conductance $G$ becomes negative, self oscillation begin to build up at the resonant frequency of the circuit formed by $L$ and $C$ and thus the super-regenerative period starts. In the beginning, the oscillations build up linearly till the time $T_L$ when the amplitude of the oscillation is large enough for limitation to begin due to curvature of the tubes characteristic. Thus the mode of the oscillator's operation till $T_L$ is essentially linear after which it changes to logarithmic. As the oscillation amplitude further increases, the conductance steadily decreases to zero (13). On reaching zero it remains there until the end of the super-regenerative period, during which
time the oscillations are maintained at their equilibrium amplitude. At the end of the super-regenerative period, the conductance becomes positive and the oscillations are damped out till the next quench cycle. The damping during the quench cycle should be sufficient to reduce the self-oscillations below noise level before the build up starts again otherwise the oscillator settles down in the coherent state.

The maximum sensitivity occurs exactly at the time when the total conductance $G$ goes from positive to negative at $t = 0$. The signal voltage across the circuit at this instant plays the greatest role in the determination of the time at which the amplitude of the self-oscillations attains its equilibrium value. An element of signal occurring before time $t = 0$ has time to decay before build up starts and, consequently, has less effect than a similar signal occurring at $t = 0$. An element of signal, arriving later than this instant, again has less effect because part of the build-up has expired before its arrival. The signal is, therefore, sampled for a short period in each quench cycle. Over the greater part of the cycle, the signal has a negligible effect. The way in which the sensitivity varies with time depends upon the nature of quench and upon the tube's and circuit parameter's. In the logarithmic mode the amplitude of the oscillation envelope is always the same. The signal advances the apparent starting time of the oscillations thus increasing the area under the envelope as shown in Fig. (5.1 d). Thus the area of the envelope changes with the amplitude of the signal. A suitable detector circuit converts this once more into a change of amplitude.
Now we calculate the nuclear signal induced in the coil. The nuclear spin is subjected to bursts of high r.f. power which brings about several effects.

I. The nuclear absorption during the presence of r.f. power reduces the Q of the coil and thus reduces the integrated pulse energy.

II. Any coherent nuclear precession, which may occur when $T_2$ is comparable to or greater than the quench period, will cause the r.f. bursts to be initiated earlier by nuclear signals rather than by noise. This latter effect gives rise to an increased integrated signal response.

Dean (14) suggests that the second mechanism is the dominant one for quadrupole resonance detection by the super-regenerative method. A calculation of the signal, based upon the second mechanism, has been made.

During one quench period $\tau$, the oscillator is on for time "tw" and is off for the rest of the quench period. Thus the output of the super-regenerative oscillator can be supposed to consist of a series of equally spaced pulses of equal widths. The quadrupole system is excited by the pulses and it relaxes both longitudinally as well as transversely between the time interval during successive pulses till a steady state is reached.

The quadrupole system has a magnetization $\vec{M}_0$ along the symmetry axis (Z axis) due to difference in population between $|m\rangle$ and $|m-1\rangle$ states. The magnitude of $M_0$ is given by (2,3). Let the angle through which $M_0$ is rotated by the first pulse be $\alpha$. If the angle between $\vec{M}$ and Z axis before and after the $n^{th}$ pulse is represented by $\alpha_n$ and $\alpha_n^+$.
respectively, then $a^+_1 = a$. Usually $T_1$ is much longer than the time interval between two consecutive pulses and $T_2$ is also longer or comparable with the latter. Therefore the longitudinal component of $\vec{M}$ will be in process of relaxing towards its equilibrium value $\vec{M}_0$ and the transverse component of $\vec{M}$ will be decaying during the time between the pulses. Let the angle between $\vec{M}$ and Z axis just before the second pulse be $a_2^-$. Further rotation of magnetization will depend upon the phase of the r.f. oscillations during the pulse relative to the phase of $\vec{M}$. This phase difference depends upon the conductance of the circuit during the on and off periods, the departure of the frequencies of the pulse from the resonance frequency and the past history as well. As the various parameters specifying the phase may vary from pulse to pulse, this phase difference may be assumed to be random. So the angle between $\vec{M}$ and Z axis after the second pulse will be $a^+_2 \neq a_2^- + a$. The same events take place when other pulses arrive. Thus the problem of finding out the angle between $\vec{M}$ and Z axis after the quadrupole system has been excited by a train of pulses is similar to that of a random walk in which there is a certain amount of relaxation during the period of two successive steps. In actual practice we get the integrated effect of the pulses in a certain time determined by the time constant of the phase sensitive detector. The detected output of the super-regenerative oscillator-detector $V(t)$ will consist of a steady value $\bar{V}$ and a fluctuating component $\Delta V(t)$.

\[ \therefore \quad V(t) = \bar{V} + \Delta V(t) \]
We assume that \( \Delta V(t) \) is a Gaussian variable i.e. at any time it has an apriori probability of being between \( V \) and \( V + dV \) given by 

\[
P_{(V)}(V) = \frac{1}{\sqrt{2\pi}dV} e^{-\frac{(V-V)^2}{2dV^2}}
\]

\[
\int_{-\infty}^{+\infty} P_{(V)}(V) dV = 1 \quad \text{and} \quad \int \Delta V^2 P_{(V)}(V) dV = \delta^2
\]

The signal that we measure when the time constant of the phase-sensitive-detector is \( \gamma_c \) is approx. given by 

\[
S(\gamma_c) = \frac{1}{\gamma_c} \int_0^{\gamma_c} \Delta V(t) \, dt = \sqrt{V} + \frac{1}{\gamma_c} \int_0^{\gamma_c} \Delta V(t) \, dt
\]

The square mean variance of the signal is given by 

\[
\langle \Delta S(\gamma_c)^2 \rangle = \frac{1}{\gamma_c^2} \int_0^{\gamma_c} \int_0^{\gamma_c} \Delta V(t') \Delta V(t'') \, dt' \, dt''
\]

We now assume that the fluctuations are governed by a correlation time which in our case is the same as quench period \( \tau \).

\[
\therefore \frac{\Delta V(t')}{\Delta V(t'')} = \frac{1}{|\Delta V(t')|^2} e^{-\frac{|t'|}{\tau}} = \frac{\delta^2}{e^{\frac{|t'|}{\tau}}}
\]

\[
\text{and } t = t' - t''
\]

It is easily shown that 

\[
\langle \Delta S(\gamma_c)^2 \rangle = \left( \frac{2\tau}{\gamma_c} \delta \right)^2
\]

Therefore the R.M.S. fractional noise 

\[
= \frac{2\tau}{\gamma_c} \frac{\delta}{V}
\]

A typical value of \( \tau \) and \( \gamma_c \) used in the spectrometer are \( \tau = 20 \mu \text{sec} \) and \( \gamma_c = 2.5 \text{ sec} \) which even for \( \delta = \sqrt{V} \) gives a signal to noise as high as 62500. Thus we see that the randomness in the phase-difference between \( M \) and the r.f. oscillations during the pulse has got practically no effect upon the signal under the practical operating conditions. Hence we can assume that in the steady state the angle between the
Z axis and magnetization, after a pulse, is always $a^+_s$ which relaxes to $a^-_s$ because of $T_1$ till the advent of next pulse which rotates it to $a^+_s$ again. If $M^-_s$ is the magnitude of the magnetization before a pulse, then the amplitude of the signal just after the pulse will be proportional to $M^-_s \sin a^+_s$. Now to calculate $M^-_s$ we make the following assumptions and approximations.

I. It is assumed that all pulses are of identical widths.

The rise time of a pulse depends upon the amplitude of the signal which initiates the pulse. The signal starting the $n^{th}$ pulse is proportional to magnetization before the $(n-1)^{th}$ pulse. As the magnetizations before the I, II, III, ... pulses are different, so the rise time of the corresponding pulses will also be different. In practice, the rise time of the pulse is only a very small fraction of even the shortest pulse. So we can, to a good approximation, neglect the difference in rise times as compared to the width of the pulses and assume that all pulses are of equal width.

II. It is assumed that pulses are very short as compared to $T_2$. This corresponds to the effective field in the rotating reference frame being governed only by $H_1$, so that the precession during the time r.f. pulse is applied may be referred to as pure nutation.

In the spectrometer, the value of pulse-width is about one tenth of $T_2$ even in the presence of the modulation field, so this approximation is well justified.
III. The relaxation during the pulse is neglected. The results of the pulse experiment show that the signal is independent of the external magnetic field i.e. $T_2^\ast$ for short pulse width ($\approx 10 \mu$s) and for low values of field ($\approx 5$ gauss) thus showing that the relaxation during the pulse, under these conditions can be neglected. The spectrometer was operated to satisfy these conditions.

IV. The effect of transverse components of magnetization in establishing the value of steady state magnetization is neglected.

If the magnetization $\vec{M}_1$ is rotated by the first pulse by an angle $\alpha$, the $x, y$ components of magnetization after the pulse will be proportional to $M_1^{-1}\sin \alpha$. As $\alpha \approx 0.05$ radian, these components will be negligible as compared to $Z$ component $= M_1^{-1}\cos \alpha$. Thus the main contribution to the steady state magnetization will come from the rotation and relaxation of the $Z$ component of magnetization.

V. $H_1$ is supposed to be uniform.

Note that $H$ is never uniform for a powder since $H_{1\text{eff}} = H_1 \sin \theta_1$ where $\theta_1$ is the angle between $H_1$ and the symmetry axis of $\nabla E$.

VI. Special effects due to tendency of spin systems to establish a "spin temperature" in the rotating reference frame are neglected (15).

Now we calculate the value of the magnetization in the steady state within the frame-work of these approximations.
Suppose a pulse of width $t_w$ is applied at the time $n\gamma$. Let the Z component of magnetization $M_z$ before the pulse be represented by $M_{z}^{-}(n)$ and after the pulse by $M_{z}^{+}(n)$. If $M_z$ obeys the equation

$$\frac{dM_z}{dt} = \frac{M_0 - M_2}{T_1}$$

then it can be shown that

$$M_{z}^{-}(n+1) = M_0 - \{ M_0 - M_{z}^{+}(n) \} e^{-\gamma/T_1} \quad (5.1)$$

and

$$M_{z}^{+}(n) = M_{z}^{-}(n) \cos \alpha \quad (5.2)$$

where $\alpha$ is the angle through which $M_{z}^{-}(n)$ is rotated by the $n^{th}$ pulse.

Now we consider the value of $M_{z}^{+}(n)$ where $n = 0, 1, 2, 3 \ldots$ to form a suitable expression for $M_{z}^{-}(n)$.

**I^{st} pulse:**

$$M_{z}^{-}(1) = M_0$$

$$M_{z}^{+}(1) = M_0 \cos \alpha.$$  

**II^{nd} pulse:**

By putting $n = 1$ in (5.1)

$$M_{z}^{+}(2) = M_0 (1 - e^{-\gamma/T_1}) + M_0 \cos \alpha e^{-\gamma/T_1}.$$ 

By (5.2)

$$M_{z}^{-}(2) = M_0 \cos \alpha (1 - e^{-\gamma/T_1}) + M_0 \cos^2 \alpha e^{-\gamma/T_1}.$$ 

**III^{rd} pulse:**

$$M_{z}^{-}(3) = M_0 (1 - e^{-\gamma/T_1}) + M_0 \cos \alpha (1 - e^{-\gamma/T_1}) e^{-\gamma/T_1} + M_0 \cos^2 \alpha e^{-\gamma/T_1}.$$ 

and

$$M_{z}^{+}(3) = M_0 \cos \alpha (1 - e^{-\gamma/T_1}) + M_0 \cos^2 \alpha (1 - e^{-\gamma/T_1}) e^{-\gamma/T_1} + M_0 \cos^3 \alpha e^{-\gamma/T_1}.$$
$4^{th}$ pulse:

$$M_{2}^{z(n)} = M_{0} - (M_{0}^{+} \omega) e^{-\gamma T}$$

$$= M_{0}(1 - e^{-\gamma T}) + M_{0} \cos \alpha (1 - e^{-\gamma T}) e^{-\gamma_{1} T}$$

$$+ M_{0} \cos^{2} \alpha (1 - e^{-\gamma T}) e^{-2\gamma T_{1}} + M_{0} \cos^{3} \alpha e^{-3\gamma T_{1}}.$$ 

Thus the expression for $M_{z}^{n}$ forms a geometric progression with first term as $M_{0}(1 - e^{-\gamma T})$ and common ratio as $\cos \alpha e^{-\gamma T_{1}}$. 

$\therefore M_{z}^{(\text{steady state})} = \text{sum of geometric series as } n \to \infty$

$$= M_{0}(1 - e^{-\gamma T}) / 1 - \cos \alpha e^{-\gamma T_{1}}$$

Due to assumption IV, $M_{z} = M_{s}$. 

$\therefore$ the amplitude of the induction signal just following the pulse is

$$\frac{M_{0}(1 - e^{-\gamma T}) \sin \omega_{s}}{1 - \cos \alpha e^{-\gamma T_{1}}}$$

This signal decays with a time constant $T_{2}^{*}$ during the time $\tau - t_{w}$ and initiates the r.f. oscillations of the next pulse at the end of the quench period $\tau$. However the effect of the assumption VI is to introduce an uncertainty in the effective zero of time for the Gaussian decay of the induction signal (16). Thus the time interval $\tau - t_{w}$ is replaced by $\tau'$ where $\tau'$ lies in between $\tau - t_{w}$ and $\tau$. So the nuclear signal that initiates the r.f. oscillations is

$$V_{s}(H_{1}, \tau) = \frac{M_{0}(1 - e^{-\gamma T}) \sin \omega_{s}}{1 - \cos \alpha e^{-\gamma T_{1}}} e^{-\frac{\tau^{2}}{2T_{2}^{2}}}$$ (5.3)

Now, knowing the nuclear signal that initiates the r.f. oscillations, we can calculate the voltage of the signal given by the spectrometer. Figure (5.2) shows the build up envelope, after time $T_{u}$ (Fig. 5.1), in greater detail. The two curves represent
the build up from two voltages $V_1$ and $V_2$. $V_1$ is the voltage reached at time $T_L$ by the oscillations building up from a sample of noise in the sensitive period, earlier in the cycle. $V_2$ is due to signal plus noise. For the time being, we are considering the events in a single quench cycle. Although the noise voltage $V_1$ is indeterminate for a single cycle, its r.m.s. value is given by

$$V_1 = \sqrt{\left(V_n^2\right)} \mu_L$$

and

$$V_2 = \sqrt{V_n^2 + V_S^2} \mu_L$$

where $V_n^2$ is the mean square noise at input, $V_S$ is the signal input, and $\mu_L$ is the voltage gain during the interval of linear build-up i.e. from the instant build-up starts to $T_L$. For simplicity, let us take the build up curves to be truly exponential in form until they are suddenly limited at the equilibrium value $V_m$. As we are starting with the values of voltages at $t = T_L$, we shall hence-forth measure time from this point and not from the beginning of the true build-up period. As $V_2$ is even less than one-hundredth of $V_m$, the difference in area to the left of vertical axis is negligible. Thus the incremental area to the right of axis (shaded in Fig. 4.2) represents the increase in output due to signal during a single cycle of quench.

Referring to Fig. (5.2)

$$V_m = V_1 e^{\frac{t_{\gamma_0}}{\alpha}} = V_2 e^{\frac{t_{\gamma_0}}{\alpha}}$$
where \( t_1 = a \ln \frac{V_m}{V_1} \) and \( t_2 = a \ln \frac{V_m}{V_2} \).

Hence the incremental area is given by

\[
\Delta A = V_2 \int_0^{t_2} e^{t/a} \, dt + V_m(t_2 - t_1) - V_1 \int_0^{t_1} e^{t/a} \, dt
\]

\[
= a \left[ V_m \ln \frac{V_2}{V_1} - (V_2 - V_1) \right]
\]

(5.4)

For signals greater than noise, the first term in the bracket is of the order of \( V_m \) whilst the second is much smaller.

Thus we can write

\[
\Delta A \approx a V_m \ln \frac{V_2}{V_1}
\]

\[
= a V_m \ln \left( \frac{V_n^2 + V_s^2}{V_n^2} \right)^{V_2/2}
\]

As the 1.5 cycle narrow-band width amplifier and the phase-sensitive detector used in the output stage of the spectrometer, allow only a very narrow spectrum of noise to effect the final signal, so we can assume that \( V_s^2 \gg V_n^2 \). Thus

\[
\Delta A \approx a V_m \ln \frac{V_s}{\left( \frac{V_n^2}{V_m} \right)^{V_2}}
\]

The final signal voltage as recorded by the spectrometer will be

\[
V = \frac{K}{T} a V_m \ln \frac{V_s}{\left( \frac{V_n^2}{V_m} \right)^{V_2}}
\]

(5.5)

where \( T \) is the quench period and \( K \) is a constant of the spectrometer determined by the detector, amplifiers, etc. The presence of \( T \) in the denominator of 5.5 is because of the fact that \( \Delta A \) is the increase in area of a single pulse and the voltage \( V \) is the integrated effect of \( \frac{T}{T_c} \) pulses where \( T_c \) is the time constant of the phase-sensitive-detector.
As \( \tau \) is a variable quantity, it has been separated from the constant \( K \).

Substituting the value of \( V \) from (5.3) into (5.5),

\[
V = \frac{B}{\tau} \ln f(\tau) - \frac{B}{\tau} \frac{\tau^2}{2\tau^2_2}
\]

(5.6)

where

\[
f(\tau) = \frac{M_0 (1 - e^{-T/\tau_1}) \sin \frac{\pi \tau}{\tau_1}}{1 - \cos e^{-T/\tau_1}}
\]

and \( B \) is the constant of the spectrometer.

In Chapter IV the following empirical formula was obeyed

\[
\frac{1}{T_2 + 2} = A + K \gamma^2 H^2 \]

Here \( H \) is the modulation magnetic field given by \( H_m \cos \omega_m t \), substituting the value of \( T_2^* \) in (5.6)

\[
V = \frac{B}{\tau} \ln f(\tau) - \frac{B}{\tau} \left( \frac{\gamma^2 + \frac{\gamma H_m - \tau^2}{2}}{2} \right) - \frac{B}{\tau} \frac{\gamma^2 H_m - \tau^2}{4} \cos 2 \omega_m t
\]

(5.7)

A strong signal was observed when the phase-sensitive detector was tuned to \( 2\omega_m \). According to equation (5.7) it is given by

\[
V(2\omega_m) = -B \gamma^2 H_m \frac{\tau^2}{4} \tau
\]

(5.8)

The results obtained with the spectrometer have been discussed in Chapter VII on the basis of equation (5.8) and the data of Chapter IV.
VI. THE DESCRIPTION AND WORKING OF THE "SUPER-REGENERATIVE SPECTROMETER"

A block diagram of the super-regenerative spectrometer is given in Fig. (6.1) and its photograph has been shown in Fig. (6.2).

A. The Oscillator

The circuit diagram of the oscillator, detector and integrator together with the circuit that allows the quench voltage applied to the oscillator has been shown in Fig. (6.3).

The basic circuit was designed by Dean (14) for use in the region of 30 MC/sec. The present circuit has been taken from McCall's thesis (17) after suitable modification.

The oscillator is the grounded-plate version of the Colpitt's oscillator. The quenching action is as follows: The two halves of the 6J6(V1), in parallel, have their cathodes tied to the cathode of the oscillator tube V2. The plates of V1 are bypassed for r.f. When a positive pulse from the external quenching circuit is applied to the grid of V1, the additional cathode bias shuts off V2. Thus the oscillator is operating only during that part of the quench during which V1 is no conducting.

At the time V2 is cut off, the cathode impedance is shunted across part of the tuned circuit. This large positive conductance shortens the decay time-constant of the tank circuit and aids in quickly damping out the free oscillations.
6.1 THE SUPER-REGENERATIVE SPECTROMETER
The Super-regenerative Spectrometer.
FIG 63 OSCILLATOR, DETECTOR AND INTEGRATOR
It is important that this impedance should not have any damping effect during the on-period of the oscillator and to ensure this, the grid of $V_1$ must be very negative (of the order of $-120$ volts). A fixed bias that can be set from $0-90$ volts is provided by a battery and potentiometer (shown in the quench circuit). The over-all positive to negative swing of the quench voltage is about $120$ volts.

The frequency of the oscillator is changed by driving the tuning condenser slowly by a motor. The motor drive can be replaced by connecting a variable-capactiy diode in parallel with the tuning condenser as shown by dotted line in the circuit diagram. The sawtooth has a period of about $5 - 10$ minutes.

A variable capacity-divider, following the tank circuit, allows some control of the fraction of the tank voltage applied to the grid of the infinite impedance detector $V_3$. The output from the cathode of $V_3$ is fed into a four section, RC filter network which integrates the pulse area. Part of the detector's output is fed to a cathode follower $V_4$ whose output is displayed on an oscilloscope. The on-off time of the oscillator is measured from this wave-form.

B. The Quenching Circuit

The circuit diagram of the quenching circuit is given in Fig. (6.4). The input to the circuit is provided by a Hewlett-Packard audio oscillator (Model 200 DR). The frequency of the input varied from $10$ K.C./sec to $70$ K.C./sec.

The tubes $V_1$ and $V_2$ square the sine-wave input. They are followed by a differentiating network. The resulting positive
and negative pips appear at the grid of $V_3$ which has a fixed negative bias, well below the cut-off. Therefore only the positive pip affects the tube current.

The output pip from $V_4$ triggers the "one-shot" multi-vibrator formed by $V_4$ and $V_5$. With no input, $V_4$ is cut off and $V_5$ is conducting. $V_4$ and $V_3$ have a common plate load. Thus the positive pip at the grid of $V_3$ appears as a negative pip at the plate of $V_4$ and the grid of $V_5$, initiating the change to metastable state. The duration of this state is determined by the $R$ and $C$ values in the grid of $V_4$ and the setting of the potentiometer in the grid of $V_4$. The output, taken from either plate, is a square wave in which the duration of the positive and negative portions may be varied. The multi-vibrator's output, after having been amplified by $V_6$ is biased by a 90 volt battery and then applied to the grid of the quenching tube. The potentiometer in the bias battery circuit is found to have a fine control over the on-off time of the oscillator.

C. The Frequency-Divider

The circuit diagram of the frequency-divider is shown in Fig. (6). The tubes $V_1$ and $V_2$ convert the input sine wave to a square wave which triggers a bistable multi-vibrator formed by tubes $V_3$ and $V_4$. The output of the multi-vibrator is a square wave of half the frequency of the input. The tubes $V_6$ and $V_7$ together with the L.C. filters allow only the fundamental sine wave to pass to the output stage which is a cathode follower formed by tube $V_8$. Thus the output of the cathode-follower is a sine wave of half the frequency of the input sine wave.
FIG 6.5 FREQUENCY DIVIDER
tube $V_5$ isolates the multi-vibrator from the filter stages.

D. The Audio Amplifier

The audio amplifier is a modified version of Metropolitan Vicker's Main Amplifier. Its circuit diagram has been given in the Appendix. It has an overall gain $= 3.7 \times 10^3$. It has a bandwidth from 10 cycles/sec to 300 cycles/sec. This bandwidth is because of the capacitors $c_1$ and $c_2$.

E. The Phase Shifter

The circuit diagram of the phase shifter is given in the Appendix. It changes the phase from 0 to $320^\circ$. However, the output signal changes with the setting of phase. Thus with each setting of phase, the input to the phase shifter has to be adjusted for constant output.

F. The Phase-Sensitive Detector

The circuit diagram of the phase-sensitive detector as shown in Fig. (6.6) is due to Schuster (18). The circuit consists of a pentode tube $V_1$ the plate load of which is switched alternately to $R_1$ and $R_2$ by the reference signal. The input signal at the grid of the pentode establishes a plate current $i = g_m e_g$ and the switching tube ($V_2$) determines which of the two resistors $R_1$ or $R_2$ will be traversed by the current. This is accomplished by a reference voltage about 30 volts in the secondary of $T_1$ applied to grids of $V_2$, alternately cutting off one-half of the tube and causing the other half to conduct. The switch tubes ($V_{2a}, V_{2b}$) have a resistance of about 7000 ohms.
FIG 6.6 PHASE SENSITIVE DETECTOR
where as the pentode $V_1$ has a resistance of 1.5 Meg ohms. This feature assures the balance stability of the circuit relative to variations in switching tube characteristics or reference voltage.

Long time constants following the detector are obtained by feeding the d.c. output to a pair of cathode followers ($V_3$, $V_4$) through the appropriate R-C elements.

G. The power amplifier used is Bogon's Model M03o booster amplifier. The narrow bandwidth amplifier is White's Operational Selective Amplifier Model 236A together with White's twin T of type 546.

H. The Helmholtz Coils

Each coil has 1350 turns and a resistance of 30 ohms. Their mean radius as well as the distance between their centres is 7 inches. A calculation shows that the peak value of the magnetic field at the centre of the coils is given by $0.096 \times i$ gauss where $i$ is the r.m.s. value of the alternating current following through the coil in milli-amperes.

I. Working of the Spectrometer

To achieve a good filling factor, the coil of the oscillator is placed directly into the sample (para-di-chloro-benzene) kept at the centre of the Helmholtz coils. The oscillators frequency is slowly changed by deriving the tuning condenser by a motor. The passage of the deriving frequency through the resonance should be "slow adiabatic". This requires $\frac{dy}{dt} \ll (\xi y)^2$
where $\delta \nu$ is the line width in frequency units.

During the experiment, oscillator's frequency was driven at the rate $3.290 \text{ KC/sec}^2$. Thus the aforesaid condition is well satisfied as the line width is about $50 \text{ KC}$. Also the total time taken by the deriving frequency to cross the line should be at least several times the time constant of the phase-sensitive detector. At the same time a good signal-to-noise ratio requires the time constant to be as large as possible. A time constant of $5 \text{ sec}$ was found to be a good compromise between these requirements. As the frequency passes through the resonance, the nuclear signal is induced across the coil. To record the resonance the signal is modulated by a sinusoidal magnetic field of $82.5 \text{ c.p.s.}$ and having a peak value about $5 \text{ gauss}$. As the Zeeman splitting of the pure quadrupole levels depends upon the orientation of the electric field gradient axis with respect to the magnetic field and this orientation being random in case of powder sample, the resonance is smeared twice a cycle by the modulating magnetic field. Thus the signal appears at the second harmonic of the modulation frequency i.e. at $165 \text{ c.p.s.}$ as the output of the integrator. This signal after being amplified by the audio-amplifier and the narrow-band-width amplifier appears at the input of phase-sensitive detector. The band-width of the amplifier is only $2 \text{ c.p.s.}$, so it cuts down the noise considerably. The noise is further cut down by the phase-sensitive detector. The reference signal for the phase-sensitive detector is provided by a Hewlett Packard Audio oscillator Model 200 AB through a phase shifter. To keep the phase difference between the two signals feeding the phase-sensitive detector constant,
the same audio oscillator provides the modulation signal. As the frequency of the modulation signal is half of the reference signal, so the audio oscillator feeds a frequency divider which halves the frequency and then drives a power amplifier. The power amplifier supplies current to the modulation Helmholtz coils. The maximum current obtained was 400 milli-amperes. The value of the current usually used for modulation was \(30 - 50\) milliamperes. The output of the phase-sensitive detector is recorded by E sterline-Angles D.C. milliammeter Model AW. The signal as recorded by the ammeter is maximum when the nuclear signal is in phase with the reference signal. This is done by setting the phase shifter. The field modulation has been used to avoid the response of the spectrometer to spurious signals which were previously observed in a self quenched frequency modulated oscillator. The frequency spectrum of the oscillator is very complicated. Because of quenching, it consists of a central frequency with side bands on either sides separated by the quench frequency. The best way to locate the central frequency is to switch off the audio oscillator feeding the quench generator so that the oscillator is operating continuously. Then its frequency can be easily measured by a receiver. The central frequency of the quenched oscillator, which is very close to this frequency is finally determined by switching on the audio-oscillator and changing the quench frequency. It is only the central frequency that does not shift by changing the quench frequency. This fact locates the central frequency.
J. Measurements

The amplitude of the signal was measured as a function of the quench frequency and the modulation current. Then, for a particular quench frequency and modulation current, the signal was measured as a function of the on-off time of the oscillator. The results have been given in the next section. These measurements were taken at room temperature.
VII. RESULTS OBTAINED WITH THE SPECTROMETER

The spectrometer was operated with low modulation field (\( \approx 3 \) gauss) so as to satisfy most of the conditions under which the theory for the spectrometer was developed in Chapter V.

Figure (7.1) shows the amplitude of the signal as a function of the pulse width (on-time of the oscillator) for the various values of the quench frequency. Three effects are quite prominent.

I. The amplitude of the signal goes through a broad maxima as the pulse width is increased.

II. The maxima becomes broader as the quench frequency is decreased.

III. In the regions of maxima, the amplitude of the signal increases with the quench frequency.

The following explanation for the result can be given.

The theory of the spectrometer was based on the assumption that the mode of the oscillator's operation is always logarithmic and the pulses are rectangular i.e. the rise and fall time of the pulse is negligible as compared to its flat portion. For short pulse widths (\( \approx 5 \mu \)sec), neither of these approximations hold and in the limit of very short pulses the spectrometer should be operating in the linear mode. In the linear mode the spectrometer output will be proportional to \( V_s \) instead of \( \ln V_s \) as in logarithmic mode and increasing pulse width should give increasing signal. As the pulse width is further increased we
FIG 7.1 SIGNAL VS. PULSE-WIDTH

I. 60 KC ($T=16.68\mu$Sec)
II. 55 KC ($T=18.18\mu$Sec)
III. 50 KC ($T=20\mu$Sec)
IV. 45 KC ($T=22.22\mu$Sec)
V. 40 KC ($T=25\mu$Sec)
VI. 35 KC ($T=28.57\mu$Sec)
come across such values of pulse width for which the spectrometer operates between the linear and logarithmic modes and the signal goes through a broad maxima over a certain range of pulse width. In this plateau, the signal as predicted by the equation (5.8) should vary as \( \frac{1}{\tau} \) independent of \( \tau' \) or \( t_w \). Note that the dependence of signal upon \( \tau' \) holds only in the logarithmic mode. Figure (7.2) shows a plot of the signal versus \( \frac{1}{\tau} \) for the various values of pulse width, conforming this prediction. A plot of the signal against \( \frac{1}{\tau} \) for different values of \( (\tau - t_w) \) also, gives the same result.

On the right side of the plateau, the spectrometer operates in the logarithmic mode because now the pulse width is quite large as compared with the rise time and the pulses can be assumed to be rectangular. In this region the theory predicts that the signal is proportional to \( \tau'^2 \). The exact value of \( \tau' \) is not known but it should lie between \( \tau \) and \( \tau - t_w \). As the value of \( \tau' \) decreases by increasing the pulse-width, therefore the signal drops for longer values of pulse-width. However, the decrease in signal amplitude is faster than predicted by the theory. This is most probably because of the changes in the tube parameters with the increase of the on-time of the oscillator. This factor may also contribute to the existence of a definite plateau for long \( \tau \), rather than a curve with a simple maximum. In addition to this, the condition that the time decay constant of the r.f. oscillations should be quite large as compared with the off-time of the oscillator, is also not satisfied for long pulses.
FIG 7.2. SIGNAL VS. QUENCH FREQUENCY
Figure (7.3) shows the signal against the r.m.s. value of the modulation current. The peak value of the modulation field in gauss can be obtained by multiplying the r.m.s. value of the current in milli-amperes by 0.097. At low fields (~ 2.5 gauss) the signal is proportional to the square of the field as predicted by the equation (5.8). As the field is further increased, the signal increases less rapidly than that given by $H^2 m$ and it finally begins to drop after passing through a broad maximum at about 10 gauss. The decrease of the signal at the high values of field can be explained by considering the effects which attenuate the amplitude of the free induction signal as discussed in Chapter IV.

The best operating conditions of the spectrometer can be summarized as follows.

I. It was found experimentally that the spectrometer is most sensitive when the noise in the detector's output, at the instant when the oscillations are building up, can be seen on the oscilloscope. This can be achieved by adjusting the controls of the quench generator to a proper on-time of the oscillator. This adjustment is quite easy to make because a part of the detector's output is always displayed on the oscilloscope.

II. The frequency of the quench generator should be high (50 - 100 KC/sec). At the high quench frequency, the region in which the spectrometer can be operated for maximum signal is very narrow. So care should be taken in selecting a proper on-time of the oscillator. A good indication of the proper time is obtained by step I.
FIG 7-3 SIGNAL VS. MODULATION FIELD.
III. The peak value of the modulation magnetic field should be about $5 - 7$ gauss for chlorine $35$ nuclei in Para-di-chlorobenzene. For other systems, the optimum modulating field will depend on $T_2$ and on the nuclear gyromagnetic ratio $\gamma$.

The other operating conditions of the spectrometer have been described in Chapter VI while discussing the working of the spectrometer.
FIG.A2 AUDIO AMPLIFIER

ALL TUBES 12AX7
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