MEASUREMENT OF NUCLEAR MAGNETIC MOMENTS
BY A MAGNETIC RESONANCE SPECTROMETER

by

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A THESIS SUBMITTED IN PARTIAL FULFILMENT OF
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ABSTRACT

A recording nuclear magnetic resonance spectrometer has been built and is in operation.

The instrument is based upon a simple oscillating-detector of original design, for which the author presents a complete analysis of sensitivity and signal to noise ratio. This analysis is based upon the van der Pol oscillator and contains a theoretical estimate of the modulation noise in such an oscillator. Comparison with other methods shows the ultimate sensitivity of the oscillating detector to be the same as that obtainable by bridge methods, but the former is much more flexible. Although similar instruments are apparently in use, no details are given in the literature.

Other features of the spectrometer are a 1200 lb. electromagnet and a lock-in detector of great stability.

Some of the resonances recorded by the spectrometer are discussed. These are:

(a) Cu$^{63}$ in the wire of the detector coil.
(b) Br$^{79}$ and Br$^{81}$ in NaBr and KBr solutions.
(c) I$^{127}$ in NaI and Ki solutions.
(d) Sb$^{121}$ in SbCl$_{5}$ and HSbCl$_{6}$.

The copper signal provides a criterion of the sensitivity of the spectrometer. The measurement of the resonant frequency agrees with values reported by Knight for metallic copper.
The resonance widths of the bromine isotopes are ten-fold narrower than values given by Pound, an important discrepancy since it throws doubt upon our ability, at present, to calculate quadrupole moments from nuclear magnetic resonance. The iodine width in NaI agrees with Pound's value.

The antimony resonance in H$_2$SbCl$_6$ confirms work of Proctor (private communication). The resonant frequency in SbCl$_5$ is about 0.07% higher. This shift is an example of the chemical effect recently discovered for fluorine and nitrogen isotopes.
THE UNIVERSITY OF BRITISH COLUMBIA
FACULTY OF GRADUATE STUDIES

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of

THOMAS LEGEAR COLLINS
B.A. (University of British Columbia) 1942
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PREFACE

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Finally, I wish to thank the University of British Columbia for the opportunity and honour of being one of its first Ph.D. candidates.

T. L. Collins

April, 1950.
TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Introduction</td>
<td>1</td>
</tr>
<tr>
<td>Chapter 1. The phenomenon of nuclear induction</td>
<td></td>
</tr>
<tr>
<td>Nuclear paramagnetism</td>
<td>5</td>
</tr>
<tr>
<td>The simple induction experiment</td>
<td>6</td>
</tr>
<tr>
<td>Bloch's equations</td>
<td>8</td>
</tr>
<tr>
<td>The reaction on the driving coil</td>
<td>10</td>
</tr>
<tr>
<td>Relaxation times</td>
<td>11</td>
</tr>
<tr>
<td>Transient phenomena - &quot;wiggles&quot;</td>
<td>13</td>
</tr>
<tr>
<td>Chapter 2. Experimental methods</td>
<td></td>
</tr>
<tr>
<td>List of methods</td>
<td>15</td>
</tr>
<tr>
<td>Comparison of methods</td>
<td>16</td>
</tr>
<tr>
<td>Quantitative consideration of simple voltage measurement</td>
<td>17</td>
</tr>
<tr>
<td>The autodyne or oscillating detector</td>
<td>20</td>
</tr>
<tr>
<td>Chapter 3. The recording nuclear magnetic resonance spectrometer</td>
<td></td>
</tr>
<tr>
<td>The oscillating detector</td>
<td>25</td>
</tr>
<tr>
<td>sensitivity</td>
<td>27</td>
</tr>
<tr>
<td>signal to noise ratio</td>
<td>29</td>
</tr>
<tr>
<td>details of construction</td>
<td>31</td>
</tr>
<tr>
<td>The lock-in detector</td>
<td>32</td>
</tr>
</tbody>
</table>
Rest of the apparatus 33

Chapter 4. The magnet and its controls
Magnet design 35
Current control 37
Proton stabilization 38

Chapter 5. Measurements and standards
Choice of sample 39
Operation procedure 40
Measurement of frequency 41
Calculation of spin 41
Calculation of magnetic dipole moments 42
Calculation of electric quadrupole moments 44

Chapter 6. Results
\( \text{Cu}^{63} \) from copper in the driving coil 45
Magnetic moment of \( \text{Sb}^{121} \) 47
Line widths of \( \text{Br} \) and \( \text{I} \) 49

Appendix I. An estimation of noise in a van der Pol oscillator 52
Appendix II. Table of nuclear resonances 57
References 60
<table>
<thead>
<tr>
<th>Figures</th>
<th>Description</th>
<th>Facing Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>Meter recording of Na\textsuperscript{23} resonance.</td>
<td>13</td>
</tr>
<tr>
<td>6 - 7</td>
<td>Oscilloscope pattern from protons.</td>
<td>13</td>
</tr>
<tr>
<td>11</td>
<td>Block diagram of apparatus.</td>
<td>25</td>
</tr>
<tr>
<td>12</td>
<td>Oscillating detector circuit.</td>
<td>26</td>
</tr>
<tr>
<td>14 - 16</td>
<td>Photographs of oscillating detector.</td>
<td>31</td>
</tr>
<tr>
<td>18</td>
<td>Magnet design.</td>
<td>35</td>
</tr>
<tr>
<td>19</td>
<td>Current control for magnet.</td>
<td>37</td>
</tr>
<tr>
<td>20</td>
<td>Proton magnet stabilizer.</td>
<td>38</td>
</tr>
<tr>
<td>21</td>
<td>Recording of Cu\textsuperscript{63} from coil.</td>
<td>45</td>
</tr>
<tr>
<td>22</td>
<td>Recording of Sb\textsuperscript{121} resonances.</td>
<td>48</td>
</tr>
<tr>
<td>23</td>
<td>Recording of Br\textsuperscript{81}, I\textsuperscript{127} resonances.</td>
<td>49</td>
</tr>
</tbody>
</table>
INTRODUCTION

The attempt by physicists to understand the structure and binding forces of nuclei is based on the correlation of measurable nuclear properties. The fundamental properties which have so far been observed are:

(a) mass;
(b) charge;
(c) size;
(d) binding energy;
(e) statistics;
(f) spin;
(g) magnetic dipole moment;
(h) electric quadrupole moment.

The subject of the research described in this thesis is the measurement of nuclear magnetic moments; however, we shall use also the spin and quadrupole moment in our discussion.

Optical spectroscopy provided us with our initial knowledge of nuclear moments (K3) and continues to provide many useful values, but the accuracy is inherently low and the measurements represent the culmination of decades of technical development. A more direct measurement is given by methods using the deflection of atomic and molecular beams,
particularly when combined with resonance techniques (K4).
The resonance principle is not inherently limited to molecular beams but may be used to directly measure the nuclear paramagnetism of material in its normal state. Late in 1945, this method was successfully applied to protons almost simultaneously by Purcell, Torrey, and Pound (P7) working at Harvard, and Bloch, Hansen, and Packard (B5) at Stanford. It was quickly developed and, in 1947, yielded results of the highest accuracy (approaching one part in a million) for the ratios of the moments of the neutron, proton, and deuteron (see appendix II). At the same time, it was realized that a new tool had been developed for the investigation of the structure of the liquid and solid state, but this aspect of the subject is not discussed in detail in this thesis. The sharpness of the resonant conditions that allow such precision make the search for resonance very tedious even when guided by spectroscopic values for the moments. The first nuclear "spectrometer" which hunted automatically was developed by Pound (P4) who measured the ratio of the magnetic moments for several nuclei within the range of his apparatus. This work is now being carried on by many people and a list of nuclear magnetic moments measured by this method is to be found in appendix II.

The importance of these measurements lies in the possibility of systematic variation of magnetic moments with nuclear species. If the proton followed the laws developed for the electron (Dirac equation), we would expect it to have
a magnetic moment equal to $\frac{e\hbar}{2Mc}$, where the symbols have their usual meaning. This value, known as the nuclear magneton, has the right order of magnitude, but the proton has a magnetic moment of 2.8 nuclear magnetons; while the uncharged neutron which we might expect to have no magnetic properties has a moment of -1.9 nuclear magnetons. The precision measurements of Bloch and Anderson (see appendix II) on the ratios of the lightest elements have provided material for much theoretical speculation on the nature of nuclear forces, but it must be admitted that the success in correlating these values has been limited.

The development of the highly successful quantum theory for atoms was immeasurably aided by the existence of recurrent atomic properties summarized in the well-known periodic table. No such simple arrangement exists for nuclei. There is some indication of order in the magnetic and electric moments ($B_1$, $F_1$, $M_1$, $N_1$), but more values are required for proof. A great need at present is for values of moderate precision (one part in a thousand) for the moments of as many nuclei as possible. We are limited to those nuclei which have a spin different from zero, but this amounts to about one hundred stable species of which forty-two have now been measured by this method.

The research described in this thesis has been concerned with the development of a recording nuclear spectrometer of sufficient sensitivity to detect nuclei with small magnetic moments. The properties of nuclear paramagnetic
resonance will be described briefly with particular reference to parameters affecting the size of the signal. There follows a short discussion of methods of detection. The theory of one method is developed fully by the application of the theory of non-linear electric oscillations. This theory was used by the author to guide him in the design of a simple circuit which is the heart of the spectrometer. Following a description of the apparatus some results obtained are discussed.
Chapter 1.

THE PHENOMENON OF NUCLEAR INDUCTION

Nuclear paramagnetism

If a sample containing nuclei with a magnetic moment is placed in a strong magnetic field $H_0$, there will appear, in time, a small polarization of the sample proportional to the field strength. This arises from the tendency of the nuclear magnetic dipoles $\mu$ to align themselves with the field. The number of possible orientations is limited to $2I + 1$ where $I$ is the spin quantum number. This aligning process is disturbed by thermal motions and, since the energy involved is small compared to the thermal energy $kT$, there will be only a slightly greater number with their magnetic moment in the direction of the field than opposed to it. The vector sum of all $N$ magnetic dipoles gives the polarization of the sample $M_0 = \chi_0 H_0$ where the susceptibility is given by the Curie law

$$\chi_0 = N \frac{I+1}{I} \frac{\mu^2}{3kT}$$

At room temperatures, the values of nuclear susceptibility are of the order of $10^{-10}$ c.g.s. units, which would be completely masked by the atomic diamagnetism ($10^{-6}$ c.g.s.) in static measurements.
The simple induction experiment

The separation of nuclear susceptibility from the atomic susceptibility is accomplished by making the measurement at a frequency corresponding to a magnetic anomalous dispersion. In the stable state, the polarization $M_0$ has the same direction as the field $H_0$. On the classical picture, if we somehow disturb the sample momentarily so that $M_0$ makes an angle $\theta$ with $H_0$, $M_0$ will precess about the field direction (Figure 1.) with the Larmor frequency $\omega = \gamma H_0$ where $\gamma$ is the gyromagnetic ratio defined by $\frac{\mu}{2\hbar}$.

It requires energy to set the polarization at an angle to the field and, as this energy is gradually lost to the atomic lattice, the precession angle will decrease to zero. If, however, we disturb the sample with a small r-f. magnetic field $2H_1 \cos \omega t$ at right angles to the steady field, a stable precession will occur when $\omega$ is close to $\omega_0$. This is the resonance effect and it is very sharp. On the microscopic picture, we are inducing magnetic dipole transitions between possible orientations of the nuclear magnetic moment $\mu$ in the steady field. As Bloch (B3) points out, we can consider the classical motion of the resultant polarization of the sample because the quantum-mechanical expectation value, in its time dependence,
follows exactly the classical laws. The resonant frequencies for nuclei in a field of 10,000 gauss lie in the range from one to fifty megacycles. Resonant frequencies for atomic dipoles in the same field lie in the microwave region.

The polarization \( M_0 \) is measured by the magnitude of the transverse rotating component which appears only at resonance. To do this, we measure the r-f. voltage induced in a coil surrounding the sample with its axis perpendicular to the field \( H_0 \). This may be the coil providing the r-f. field \( H_\perp \) or it may be a separate coil, depending upon the method of detection (see chapter 2). The measurement is simplified if we produce a recurrent indication of resonance by sweeping the frequency or the field strength at an audio rate. Two methods are commonly used.

In the first (figure 2), the field is swept completely through resonance and the magnitude of the transverse polarization is observed by displaying the rectified output from the pick-up coil on an oscilloscope. If the horizontal deflection on the oscilloscope follows exactly the modulation of the field strength, we obtain a plot of the transverse component against field strength. Frequency modulation may be used in place of field modulation, but the latter is commonly used since it may be simply applied with a pair of
small coils.

The second method (figure 3), uses a field modulation much smaller than the resonance width. This produces a small modulation on the induced r-f. voltage whose amplitude depends on the slope of the resonance curve. If the frequency or field is changed very slowly, the slope may be plotted on a recording meter by the "lock-in" detector technique. Figure 5 is a reproduction of a meter tracing.

**Bloch's equations**

In order to describe the motion of \( M_0 \), Bloch (B3) introduced two "relaxation" times, \( T_1 \) and \( T_2 \), which describe the interaction of the nuclear dipoles with their environment. The component of \( M_0 \) parallel to \( H_0 \) determines the energy of the polarization. This component can only vary by absorption of energy from the driving field \( H_1 \) or by interaction with the atomic lattice. If we assume that the effect of the latter is to produce an exponential time dependence, we can describe it by the "time constant" \( T_1 \). However, the transverse components have no energy associated with them and we have the added possibility of non-energetic interactions. The field \( H_0 \) is not homogeneous and the Larmor frequency has a spread throughout the sample. Individual nuclear
components interfere and the transverse components may disappear in a time much less than $T_1$. By again assuming an exponential time dependence, we can describe this process by a transverse relaxation time $T_2$. The field inhomogeneity may arise from the presence of atomic dipoles and neighboring nuclear dipoles as well as from the magnet itself.

Using a model characterized by these relaxation times, Bloch derived a set of differential equations which give a complete description of the motions of $M_0$. These have been solved only for certain conditions, and we are interested in the case of "slow passage". The solutions are expressed in terms of $u$ and $v$, the amplitudes of the components of the transverse polarization which are in phase and out of phase with the driving field $H_1$.

\[ u = \frac{\gamma T_2^2 H_1 \Delta \omega}{1 + (T_2 \Delta \omega)^2 + (\gamma H_1)^2 T_1 T_2} M_0 \]  

\[ v = \frac{\gamma H_1 T_2}{1 + (T_2 \Delta \omega)^2 + (\gamma H_1)^2 T_1 T_2} M_0 \]  

where

\[ \Delta \omega = \omega_0 - \omega \]

Following Bloembergen (B9), we will find it convenient to consider the linear complex transverse susceptibility

\[ \chi = \chi' - j \chi'' \]

Thus $u = 2H_1 \chi'$, $v = 2H_1 \chi''$ and

\[ \chi' = \frac{1}{2} \frac{\gamma T_2^2 \Delta \omega H_0}{1 + (T_2 \Delta \omega)^2 + (\gamma H_1)^2 T_1 T_2} \chi_0 \]

\[ \chi'' = \frac{1}{2} \frac{\gamma T_2 H_0}{1 + (T_2 \Delta \omega)^2 + (\gamma H_1)^2 T_1 T_2} \chi_0 \]
The components $u$ and $v$ have the shape of dispersion and absorption curves for a damped harmonic oscillator. This was put into the equations by the assumption of an exponential form for the relaxation terms. As $H_1$ is increased, the absorption $v$ passes through a maximum and decreases to zero. On the microscopic picture, this falling off is equivalent to equalizing the populations of the energy levels by raising nuclei to higher energies faster than they can lose energy to the lattice.

The reaction on the driving coil

In most experiments we are interested in the change in the impedance of the driving coil caused by the linear transverse susceptibility at resonance. The author considers the coil as a parallel combination of an inductance $L$ and a small loss $1/R$ (figure 4), and finds the added loss $\Delta 1/R$ (absorption) and the change in inductance $\Delta L$ which appears at nuclear resonance, as seen from the coil terminals.

We may write

$$L = (1 + 4\pi q \chi) L_{\text{vac}}$$

where $q$ is the "filling factor" for the coil. Then

$$\Delta L = 4\pi q (\chi' - j \chi'') L$$

The coil impedance is given by

$$\frac{1}{Z} = \frac{1}{R} + \frac{j}{L \omega}$$

and, since the changes are very small,

$$\Delta \left(\frac{1}{Z}\right) = \frac{\partial \frac{1}{Z}}{\partial L} \Delta L = \frac{j}{L^2 \omega} \left[ 4\pi q L (\chi' - j \chi'') \right]$$
The real part of this expression is the added loss
\[ \Delta \left( \frac{1}{R} \right) = \frac{4\pi q}{L} \chi'' \]
The change in inductance is \[ \Delta L = 4\pi q L \chi' \]

Utilizing expressions (4) and (5), and \( \gamma H_o = \omega_o \approx \omega \)
\[ \Delta \left( \frac{1}{R} \right) = \frac{2\pi q}{L} \frac{T_2}{1 + (T_2 \Delta \omega)^2 + (\lambda H_1)^2 T_1 T_2} \chi_0 \]  \( (6) \)
\[ \Delta L = 2\pi q L \frac{T_2^2 \omega \Delta \omega}{1 + (T_2 \Delta \omega)^2 + (\lambda H_1)^2 T_1 T_2} \chi_0 \]  \( (7) \)
The slope of the resonance absorption \( \frac{d}{d\omega} \left( \frac{1}{R} \right) \) is recorded when using the lock-in detector technique. The measurements will be made with no saturation, that is \( (\lambda H_1)^2 T_1 T_2 \ll 1 \)
\[ \frac{d}{d\omega} \left( \frac{1}{R} \right) = \frac{2\pi q}{L} \frac{2 T_3^3 \Delta \omega}{[1 + (T_2 \Delta \omega)^2]^2} \chi_0 \]  \( (8) \)
This expression gives two peaks (figure 5) when
\[ \Delta \omega = \pm \frac{1}{\sqrt{3}} \frac{1}{T_2} \]
The value of expression (8) at its two maxima is
\[ \pm \frac{2\pi q}{L} \chi_0 (0.648 T_2^3) \]  \( (9) \)
and the relaxation time \( T_2 \) is related to the separation by
\[ \frac{1}{T_2} = \sqrt{3} \pi \times (\text{separation of peaks in cycles per second}). \]

Relaxation times

The previous development shows the strong dependence of the output on the relaxation times. Unfortunately, little is known about the mechanism of energy transfer between
nuclei and the atomic lattice. The coupling is very weak and theoretical predictions of relaxation times are much in excess of measured values. Bloembergen (B9) has calculated \( T_1 \) and \( T_2 \) by considering the frequency spectrum of the fluctuating field at the nucleus due to thermal motions of neighboring nuclear dipoles. He predicts (and has verified) that \( T_1 \) and \( T_2 \) should be equal provided the thermal motions are rapid compared to the Larmor frequency. The relaxation times for protons in pure water are of the order of seconds.

Any energetic interaction between molecules and nuclei will tend to shorten relaxation times. The addition of paramagnetic ions provides a strong coupling, and even a low concentration will greatly reduce \( T_1 \) and \( T_2 \). An electric interaction is also possible with many nuclei. If an electric quadrupole moment exists, it can react with the non-uniform electric field of the molecules giving a relaxation time inversely proportional to \( Q^2 \) and to the electric field gradient (B9). This may explain the broad resonance for some nuclei. As an example, \( ^{127}\text{I} \), which is known to have a large quadrupole moment, shows a resonance width between points of maximum slope of 14 kc; \( ^{23}\text{Na} \), on the other hand, shows a width of a few hundred cycles determined by the magnet.

The inhomogeneity in the field of the electromagnet used for these experiments gives an upper limit to \( T_2 \). If the field varies over the sample by an amount \( \Delta H_0 \),
Fig. 5.

Na\textsuperscript{23} in sat. NaI soln. 7.5 mc.

500 cycles
2 kc./min.

Fig. 6
Protons in .01 M MnSO\textsubscript{4} soln.

Fig. 7
Protons in very dilute MnSO\textsubscript{4} soln.

to face p. 13.
$T_2$ will have a maximum value of about $1/\gamma \Delta H_0$. The magnet must provide a field uniform to better than 1 gauss over the sample to avoid reducing the size of the signal. The author wishes to stress the importance of the homogeneity of the magnetic field to anyone contemplating construction of proton stabilized magnets.

**Transient phenomena - "wiggles"**

In a field of sufficient uniformity, a striking pattern appears on the oscilloscope when we sweep through resonance in a time short compared to $T_2$ (figure 6). A simple qualitative explanation is that the nuclei do not follow the rapid variation and are left precessing freely after the field has passed conditions of forced resonance. The precession frequency is determined by the instantaneous field which is steadily changing. Thus the nuclei precess at a different frequency from the r-f. field and the two frequencies produce a rising beat note, which is the "wiggle." In figure 7, the forward and back traces have been separated. The "wiggle" appears after passing through resonance, but in this picture it has not died away completely before the approach to the next resonance.

The wiggles may be useful. Jacobsohn and Wangsness (J1) showed that the pattern is perfectly symmetrical when the field is centered on the resonance. This has been used for precision comparison of magnetic moments (B7). The size of the wiggles depends strongly on the field uniformity and
this provides a sensitive method for exploring the magnetic field.
Chapter 2.

EXPERIMENTAL METHODS

In this chapter, we consider the methods of conversion of the rotating transverse polarization to audio signals. The difference in technique between various experimental groups lies in this initial stage. A description of the basic methods is given, but, for each method, a further variation exists in the amount of amplification used before rectification of the r-f. voltages. All groups use both the oscilloscope and recording meter for observation of the audio signals, as outlined in chapter 1. This chapter also contains the author's treatment of the oscillating-detector; the actual circuit details are given in the next chapter.

List of methods

The references in this list are to sources of further information and do not necessarily refer to the originator.

(a) Simple measurement of the voltage changes across the driving coil when it is fed from a constant current source.

(b) The coil in (a) replaced by a resonant cavity. (B9)
(c) A detected oscillator signal may be balanced against the audio signal in (a), cancelling the variations in oscillator amplitude. (amplitude bridge - T2)

(d) The coil may be incorporated in one arm of an r-f. bridge. (B10) (P2)

(e) An initial balance of the oscillator voltage may be obtained by placing a pick-up coil at right-angles to the driving coil. (B6)

(f) The driving coil may be the oscillator tank coil. This arrangement is similar to the autodyne detector. (used in this research)

(g) The oscillator in (f) may be quenched at an audio rate, as in the super-regenerative detector. (R1)

Comparison of methods

An important feature, common to all methods, is the presence of a relatively large oscillator signal at the r-f. detector. This "unbalance" voltage is much larger than that arising from the nuclear induction and it determines the phase of the component of the transverse polarization which is detected. Figure 8 will make this clear. \( V_0 \) is the unbalance voltage whose phase with respect to \( H_1 \) is determined by the apparatus. The signal \( V_s \) (exaggerated) has a phase dependent on detuning. It is composed of the
two components $u$ and $v$, which are in phase and out of phase with $H_1$. The rectifier detects only changes in amplitude. Thus only the component of the signal voltage in phase with $V_0$ will be detected and this may be pure dispersion ($u$), pure absorption ($v$), or a mixture of both. Circuits of type a, b, and c detect almost pure absorption, while types d, and e have an adjustable unbalance phase and may detect either component. The autodyne circuits, in which we are particularly interested, usually detect absorption but may be built so that they detect dispersion; the super-regenerative types are similar.

The ease with which a circuit can be adjusted to the desired conditions governs, to a great extent, the choice of method. For hunting unknown or poorly known resonances, it is convenient to have a circuit whose frequency can be varied over a wide range by a single control, driven by clockwork. Circuits of type (f) and (g) have this property automatically, but the bridges (d) and (e) require many simultaneous adjustments. For proton stabilization of a magnet which is not continuously varied, the amplitude bridge (c) provides a simple arrangement. For investigation of line shapes or precision measurement of nuclear moments where it is important that only pure absorption or dispersion is observed, the bridge methods are preferable.

Quantitative consideration of simple voltage measurement

Before considering the autodyne circuit in detail,
a discussion of the equations pertaining to the simple voltage measurement of type (a) will be given. It will be interesting to compare these equations with similar ones which will be derived for our circuit.

The method consists of measuring the r-f. voltage across the driving coil, the rectifier usually being isolated from the circuit by an r-f. amplifier. The circuit, which we assume to be tuned, is driven with a constant current \( i \) (figure 9). This develops a voltage \( V_o = i R_o \), where \( R_o \) is the parallel tuned impedance of the circuit. In a similar manner to that used in the last chapter, we can write

\[
\Delta L = 4\pi q (\chi' - j \chi'') L
\]

and

\[
\frac{1}{Z} = \frac{1}{R} + \frac{1}{jL\omega} + jC\omega
\]

In this case

\[
\Delta V = i \frac{\partial Z}{\partial L} \Delta L
\]

which, remembering

\[
R = QL\omega
\]

may be readily evaluated as

\[
\Delta V = iQ^2 L\omega 4\pi q (\chi'' + j\chi')
\]

As shown above, we will only detect the real part of this expression, since a large voltage of this phase is present at our detector. The current cannot be made arbitrarily large and to remove it from the expression, we use

\[
H_i = \frac{Q}{c} i \sqrt{L}
\]

where \( c \) is a constant depending on the shape of the coil.
c increases as the dimensions of the coil are increased; the size of the coil, however, is limited by the available volume of uniform field.

Thus

\[ \Delta V = 4\pi Q\sqrt{L}\omega q c H, \chi'' \]

\[ = 2\pi q c Q \sqrt{L} \omega v \]  \hspace{1cm} (11)

Both \( v \) and its derivative (used in the recording meter method) pass through a maximum as \( H_1 \) is increased. For comparison, it will be sufficient to write for the detected output:

\[ V_a = 2\pi q c Q \sqrt{L} \omega^2 \chi_o f(T_i, T_z, \chi, H_1, \Delta \omega) \]  \hspace{1cm} (12)

where the function is determined by the method of modulation.

For signal to noise ratio comparisons, it is convenient to consider the detected output from (11) without reference to the method of modulation. We also detect noise

\[ \overline{e^2} = 4kT R \Delta \nu = 4kT \Delta \nu Q L \omega \]

in each side-band determined by the bandwidth \( \Delta \nu \) of the audio system. These side-bands add quadratically giving a signal to noise ratio

\[ \frac{s}{n} = \frac{\pi q c Q'' \omega''}{(2kT \Delta \nu)^{1.2}} v \]  \hspace{1cm} (13)

which is not dependent upon the inductance of the coil. The troubles with this simple arrangement are other sources of noise. Modulation of the oscillator amplitude may be balanced out by the amplitude bridge. The rectifier contributes shot noise which is roughly proportional to the square root of the voltage detected.
Since

\[ V_0 = i Q L \omega = c H, \sqrt{L} \omega \]

it can be seen that some improvement in signal to noise ratio from this source may be gained by making \( L \) large. A better method is to provide sufficient amplification between the circuit and the detector to make the shot noise negligible. The tuned circuit would then be adjusted to give the minimum possible noise factor for the r-f. amplifier. Noise in the rectifier may be reduced still further by almost cancelling \( V_0 \) by means of a bridge network, but this is accompanied by a considerable reduction in the flexibility of the circuit.

The autodyne or oscillating detector

The autodyne detector is a weakly oscillating oscillator which shows large changes in amplitude whenever it receives a voltage of frequency near to its own. It was used in the earliest days of radio communication because of its extreme sensitivity, the name arising from the heterodyne note produced when it is almost tuned to the incoming wave. The name oscillating detector is suggested by the author for an autodyne detecting its own frequency. There is a parallel with the lock-in detector which is a zero-frequency heterodyne detector; the signal is mixed with a voltage of its own frequency.

The use of this method for the detection of nuclear induction signals was suggested by Roberts (R1) and was used independently by Pound (P4). Many others are apparently now using the same method (H1) (P8) (K1) (A2) (A1),
but few details have been published. No circuit diagrams are available and the author is not aware of any published analysis of this method of detection of nuclear resonance.

In order to understand the operation of the oscillating detector, we must inquire into the mechanism limiting the amplitude of a vacuum tube oscillator. It is well known that the equation for a harmonic oscillator contains no limitation on the amplitude of oscillation, and we may expect a vacuum tube oscillator with more than critical regeneration to have an infinite amplitude. This, of course, does not occur; the usual explanation is the added loss in the circuit when the amplitude is large enough to cause a flow of grid current. However, it is possible to adjust oscillators so that the amplitude is stable when no grid current is flowing (class A). This problem was partly solved by van der Pol in 1920, and we shall apply his result as presented in his Nonlinear Theory of Electric Oscillations (V2, 1934), to our problem.

Consider the simple triode oscillator shown in figure 10. The rate of change of the plate current is

\[
\frac{di_p}{dt} = g_m \frac{dv}{dt}
\]

where \( v \) is the voltage across the tuned circuit. The voltage induced in the tank coil is \( M g_m \frac{dv}{dt} \) the sign depending on the direction of the windings.

Now \( i_L = i_R + i_c \)

or \[-\frac{1}{L} \int (v - Mg_m \frac{dv}{dt}) dt = \frac{v}{R} + C \frac{dv}{dt}\]
or \[ \frac{d^2v}{dt^2} + \frac{1}{R} \left( \frac{v}{L} - \frac{M}{L} q_m v \right) + \frac{v}{L} = 0 \]

If \[ \dot{i}_p = \alpha' v - \frac{1}{2} \beta' v^2 - \frac{1}{3} \gamma' v^3 \]
which is non-linear, then
\[ \frac{M}{L} q_m = \frac{M}{L} \alpha' - \frac{M}{L} \beta' v - \frac{M}{L} \gamma' v^2 = \alpha - \beta v - \gamma v^2 \quad (14) \]
and
\[ \frac{d^2v}{dt^2} + \frac{1}{R} \left( \left( \frac{1}{R} - \alpha \right) v + \beta v^2 + \gamma v^3 \right) + \frac{v}{L} = 0 \quad (15) \]

This is the differential equation for the vacuum tube oscillator, assuming that three terms of a power series expansion are sufficient to describe the vacuum tube characteristic. This equation may be applied to any circuit by using for \(-\alpha\) the negative conductance that the tube places across the tuned circuit. Van der Pol solved this equation under the assumption that \(\beta = 0\), that is the tube is working about a point of inflection in its characteristic. We shall see that this condition is strictly satisfied in our circuit, but the results have some validity for other circuits since the behaviour is not strongly dependent on \(\beta\).

Van der Pol finds, for the case where the changes are slow compared to the frequency, that the amplitude \(V\)
\[ V = \sqrt{\frac{\alpha - \frac{1}{R}}{\frac{3}{4} \gamma}} \left[ 1 + e^{-\frac{1}{L} (\alpha - \frac{1}{R})(t - t_o)} \right]^{-\frac{1}{2}} \quad (16) \]
which reaches a limiting value of
\[ V = \sqrt{\frac{\alpha - \frac{1}{R}}{\frac{3}{4} \gamma}} \quad (17) \]
This equation shows how an oscillator may be used as a sensitive detector. A change of \(\frac{1}{R}\) in the tank coil, as found at nuclear resonance, or a change of feedback \(\alpha\) produces a change in the amplitude of oscillation.

The non-linear term \(\gamma\) determines the magnitude of the change in amplitude, which is the nuclear resonance
signal. This may be very large if the circuit is almost linear, a condition which cannot be obtained with normal grid leak biased oscillators. The operation of class A oscillators requires some form of automatic amplitude control (A.V.C.), since only a small change in $\alpha$ is required to raise the amplitude of oscillation from zero to the point where grid current starts to flow. The A.V.C. may control the transconductance of the tubes (and therefore $\alpha$) with a voltage obtained by rectifying the r-f. output. This will be described fully with reference to the particular oscillator used in this research.

The oscillating detector method is not limited to investigations of nuclear magnetic resonance but may perhaps be applied with profit to other physical measurements. For example, it should be possible to fill the cavity of an external cavity klystron oscillator with a gas showing microwave absorption. The amplitude of oscillation may be controlled by an A.V.C. on the grid controlling the beam current. If an almost linear oscillator can be obtained, this simple microwave spectrograph should have great sensitivity. Nor is the method limited to high frequencies. Schneider (Sl) uses an audio oscillator as both the source of a modulating voltage and a "lock-in" detector of the audio voltage after some physical measurement. He discovered that the normal limitation - the product of response time and bandwidth is approximately unity - no longer holds. This he attributes to the essential non-linear form of the equations governing the
amplitude of an oscillator.
Chapter 3.

THE RECORDING NUCLEAR MAGNETIC RESONANCE SPECTROMETER

The spectrometer built for this research is shown in block diagram in figure 11. Most of the parts follow standard electronic design; but two of them, the oscillating detector and the lock-in detector, were developed specifically for this instrument. These will be described in detail. The magnet was also designed by the author but it will be described, along with its controls, in a separate chapter.

The oscillating detector

The oscillator shown in figure 12 is the autodyne or oscillating detector used in this apparatus. This circuit was developed with the guidance of the theory given in the last chapter. The circuit is not a standard one, so the conditions for oscillation will be developed.

Figure 13 shows one tube of the push-pull pair.

\[ i = (V - V_i) \frac{j}{C} \omega \]

The voltage applied to the grid is out of phase with the voltage applied to the feedback condenser \( C_1 \). The current \( i \) flowing in this condenser is given by
Oscillating Detector.

Fig. 12.

R1 = 680K  C6 = .01 mfd.
R2 = 10K  C7 = 1000
R3 = 1.5K  C8 = 1000
R4 = 220Ω  C9 = 250
R5 = 47K  C10 = .5 mfd.
R6 = 220K  C11 two gang - 140 pf.
R7 = 10K  per section
R8 = 1Meg  L1 - tunes 5.7 - 10.3 Mc.
C1 = 2-6 ceramic.
C2 = 500  L2 - tunes at 7 Mc with
C3 = 1000  coil capacity + 3 pfs.
C4 = .01 mfd.
C5 = .01 mfd.  All tubes 6AG5

to face page 26.
The plate load of the tube is effectively only the capacity $c_2$. So $V_o = g_m V / j c_2 \omega$ 

$g_m V \gg i$

Thus $i = V (j c_1 \omega - \frac{c_1}{c_2} g_m)$

or the admittance looking into the feedback condenser is $j c_1 \omega - \frac{c_1}{c_2} g_m$

which has a negative conductance $- \frac{c_1}{c_2} g_m$.

If the two tubes are placed across a tuned circuit, oscillations will start when this negative conductance completely cancels the circuit loss. If, as usual, $1/R$ is the loss and $C$ is the total tuning capacity

$\frac{1}{R} = \frac{C \omega}{Q} = \frac{1}{2} \frac{c_1}{c_2} g_m$

So for one tube

$g_m \geq 2 \frac{c_2}{c_1} \frac{C \omega}{Q} = 2 \frac{c_2}{c_1} \frac{1}{Q \omega}$ \hspace{1cm} (18)

It is important to note that there is no reactive component of feedback involving $g_m$, resulting in frequency stability against changes in tube voltages. Since, for a given coil, $Q$ is approximately independent of frequency, the circuit may be tuned with a variable condenser over a wide range without readjustment of $C_2/C_1$.

The Van der Pol theory may be applied directly to this oscillator since push-pull circuits automatically operate about a point of inflection. The circuit was designed for stability, wide tuning range, and simplicity; and this theoretical simplicity is a bonus.

It is desirable to have as nearly linear tubes as possible; 6AG5's were the best pentodes found for this purpose.
They have the added attraction of a uniformly low noise resistance (1000 ohms), which is a great improvement over the erratic 6AK5. It should be possible to use twin triodes but results with the minature 6J6 were unsatisfactory. Careful measurements on 6AG5's showed that it is possible to vary the transconductance $\alpha'$ from 3ma/v to 7 ma/v by varying the grid bias over a 2 volt range. The third differential coefficient $\gamma'$ remains practically constant at 0.4 ma/v$^3$ during this variation. This allows us to apply the A.V.C. necessary to maintain the oscillation at a low level by varying $\alpha$ without affecting $\gamma$. To prevent loading the circuit with the non-linear crystal detector, a wide band low gain amplifier is used. The crystal is connected so that it generates negative voltage which is used to bias the 6AG5's. A network inserted in this A.V.C. lead reduces the feedback of audio voltages 20 times for all frequencies above about 30 cycles. It is necessary that all audio frequencies of interest have the same feedback factor if the detector is to have a uniform audio frequency response. The r-f. voltage may be adjusted by varying the capacities $c_1$. We usually work at about 1 volt across the whole tuned circuit: this remains constant throughout the tuning range. Under these conditions $\alpha = \frac{1}{2} \frac{c_1}{c_2} q_m \Downarrow 2 \times 10^{-5}$ varying with tuning $\gamma = \frac{1}{2} \frac{c_1}{c_2} \gamma' = 0.2 \times 10^{-5}$ (constant)

Sensitivity of the oscillating detector

The sensitivity is given by the change in output
voltage for a change \( \Delta V_{1/R} \) in the tuned circuit. We define \( m \) as the d-c. output for 1 volt across the tuned circuit \( (m=2) \), and \( b \) as the change in \( \alpha \) for a 1 volt change in output due to the A.V.C.

The voltage across the tuned circuit \( V \) is

\[
V^2 = \alpha - \frac{1}{R}
\]

so

\[
\frac{3}{2} \gamma V dV = d\alpha - d\left(\frac{1}{R}\right)
\]

Applying A.V.C.

\[
\frac{3}{2} \gamma V \Delta V = -mb \Delta V = \Delta\left(\frac{1}{R}\right)
\]

or

\[
\Delta V = -\frac{\Delta\left(\frac{1}{R}\right)}{\frac{3}{2} \gamma V + mb}
\]

The audio output voltage \( V_a \) is \( m \) times this

\[
V_a = -\frac{m \Delta\left(\frac{1}{R}\right)}{\frac{3}{2} \gamma V + mb}
\]

At small voltages

\[
\frac{3}{2} \gamma V < mb
\]

and

\[
V_a = -\frac{1}{b} \Delta\left(\frac{1}{R}\right)
\]

For a-c. changes \( b \) has a smaller value than for d-c. changes. Above 30 cycles \( b \approx 10^{-6} \) and is constant.

\( \Delta\left(\frac{1}{R}\right) \) has a maximum for \( H_1 \) near zero. Substituting from (6) with \( H_1 \) small

\[
V_a = \frac{1}{b} \frac{2\pi q}{L} \frac{T_2}{1 + (T_2 t + \omega)^2} \chi_o
\]

when the driving field \( H_1 \) is small. For the differentiated signal used in the lock-in method

\[
(V_a)_{\text{max}} = \frac{1}{b} \frac{2\pi q}{L} (0.648 T_2^2) \chi_o \delta\omega
\]

where \( \delta\omega \) is the audio magnetic field sweep - \( \delta\omega = \gamma \delta H_o \)

Finally, substituting for \( \chi_o \) from (1)

\[
(V_a)_{\text{max}} = \frac{1.3\pi q NT_2^2}{bL} \frac{T (T+1)}{3kT} \gamma^2 h^2 \delta\omega
\]
Comparison of equation (21) with (12) for the output from the simple voltage measurement shows two important differences. First, the output is increased in the oscillating detector by decreasing the inductance. Secondly, the output for a given material does not depend on the frequency, provided the tank capacity only is varied. This was verified for proton signals, which have the same size at 5mc. or 10mc. This property is useful when comparing signal sizes with the spectrometer.

The signal to noise ratio

It is desirable to compare the signal to noise ratio of this method with the simple measurement of voltage. This requires a knowledge of the noise present as a modulation on a van der Pol oscillator. This is a very difficult problem in non-linear mathematics for which a solution has not been published. An attempt by the author to evaluate this noise is contained in appendix I. The validity of a basic simplifying assumption could be verified by an exact solution, or by experiment. Such experiments have not been carried out, as yet, since they constitute, in themselves, a separate research. The solution is not inconsistent with the behaviour of the oscillating detector.

The audio noise which may be detected as a modulation on the oscillator is (equation 13, appendix I)

\[ \frac{V_n}{V} = \frac{8kT\Delta \nu}{(\frac{3}{4} \pi V^2)^2 R} \]

Since the A.V.C. feedback introduces no detuning, it has no effect on the signal to noise ratio.
The amplitude change of the oscillator in the absence of A.V.C. is
\[ \Delta V = \frac{\Delta \left( \frac{1}{R} \right)}{\frac{3}{2} \omega V} \approx \frac{4\pi q}{L \omega \frac{3}{2} \omega V} \]
and the signal to noise ratio becomes
\[ \frac{S}{N} = \frac{4\pi q}{L \omega} \frac{X''}{(Q\omega)^{\frac{1}{2}}} \frac{V}{(32kT\Delta\nu)^{\frac{1}{2}}} \]

It is desirable to remove \( V \) so that we may compare this result with the simple case. \( V \) cannot be arbitrarily large because of saturation. We can remove it by using
\[ V = i L \omega = c H_1 \sqrt{L} \omega \]
where \( c \) is the same as in (10).

This gives
\[ \frac{S}{N} = \frac{4\pi q c}{(32kT\Delta\nu)^{\frac{1}{2}}} \frac{X''}{H_1 (Q\omega)^{\frac{1}{2}}} \]

Introducing
\[ \nu = 2H_1 \chi'' \]
\[ \frac{S}{N} = \frac{\pi q c Q^{\frac{1}{2}} \omega^{\frac{1}{2}}}{(8kT\Delta\nu)^{\frac{1}{2}}} \nu \]

which has a maximum value, since the noise initially decreases faster than the signal as \( H_1 \) is raised.

Compare this to equation (13) - they differ only by a factor of two. The necessary modification of the simple circuit by an amplitude or r-f. bridge will remove this small difference. Thus the oscillating detector has the same ultimate sensitivity as the simple voltage measurement across a driving coil fed with a noiseless current.

The oscillating detector is a much simpler circuit. For equivalent performance, the "simple" measurement requires: a separate oscillator, a tuned driving coil, an amplitude or r-f. bridge, an r-f. amplifier, and a detector. The number of controls for continuous frequency variation is much larger than the single one required for the oscillating detector.

As pointed out in the appendix, the noise factor of the tubes must be taken into account. This factor depends on
the tuned circuit impedance and the frequency, but not strongly. It is also convenient to have the noise and the signal from the oscillating detector large enough that no special care need be taken with subsequent audio amplifiers. These considerations, together with the practical limitation of available tuning condensers of sturdy construction, determine the inductance of the oscillator tank coil. The inductance will generally be smaller than average practice. In our circuit, the limitation was imposed by the available tuning condenser; an increase in sensitivity with a slight reduction in signal to noise ratio should be possible by doubling its size.

Details of construction

The oscillating detector is housed in a rigidly constructed box to reduce microphonics (figures 14 & 15). This box sits between the magnet coils and the tubes are oriented so that the stray field will have the least effect on their beam current. The tank coil is housed in a small box (figure 16), connected to the main chassis by 1/2" brass tubes which carry the leads. The tank coil consists of 40 turns on a thin walled lucite form, 1/2" long. Samples are placed in 10 mm. test tubes, which fit snugly into the coil form. The sides of the coil box carry the field modulation coils.

The frequency of the oscillator is adjusted by a single control which can be driven by a synchronous motor and adjustable gear train. The slowest speed, which is often used,
is one complete revolution in 60 hrs. With the coil described, the frequency range is 5.7 to 10.4 mc.

The lock-in detector

The block diagram shows the relative position of the lock-in detector. It converts the amplified audio signal, which appears in the small sweep method (figure 3), into a d-c. voltage which is recorded by the vacuum tube voltmeter and recording meter. A lock-in detector is a zero frequency heterodyne detector which has the important properties of responding to only a narrow band of frequencies centered on the local oscillator frequency, and of responding proportional to the cosine of the phase angle between the signal and local oscillator voltages. For this apparatus, a necessary property is extreme stability of the zero signal d-c. output voltage.

The circuit in figure (17) which was developed for

this apparatus has a stable zero signal voltage of less than 0.005 volts independent of the size of the local oscillator signal. The four crystal diodes form a diode switch. When the local oscillator signal reaches its peak all four diodes conduct simultaneously, effectively shorting the input condenser to ground for a fraction of a cycle. When properly phased, this switching action converts the incoming signal to a d-c. voltage with a ripple of equal size. The ripple is
removed by an adjustable time constant (0.1, 0.3, 1, 3, 10 sec.) which also determines the bandwidth of the whole apparatus. The distinctive feature of this circuit is the use of a pen-light cell for diode bias; normal resistance-capacity bias has a much poorer stability.

Rest of the apparatus
The remaining parts of the spectrometer follow conventional designs.

(a) The amplifier contains two sections, each a two tube feedback amplifier with cathode follower output. Change of gain is accomplished by feedback switching; the overall gain is 30 to 100 db. adjustable in 10 db. steps.

(b) The vacuum tube voltmeter is described on page 480 of Valley and Wallman (VI). It is very satisfactory and provides full scale ranges of 0.1, 0.3, 1, 3, and 10 volts on the recording Esterline-Angus 1 ma meter.

(c) The sweep and local oscillator are provided by a Hewlett-Packard audio oscillator with suitable matching transformers.

(d) Power for the oscillating detectors and the amplifier is supplied by a vacuum tube regulated power supply. Filament power comes from storage batteries.

(e) Frequency measurements are made by a General Radio type 620-A heterodyne frequency meter, often with the aid of a communications receiver.

All apparatus is housed in a shielded cage. The high r.f. noise level in this building makes this necessary.
The cage also provides freedom from interference by neighboring spectroscopic arcs.
Yoke constructed from hot rolled steel bolted together.

Cross-section of coil.

1200 lb. MAGNET.

FIG 18.
Chapter 4.

THE MAGNET AND ITS CONTROLS

The magnet used for nuclear spectroscopy costs as much as all the rest of the spectrometer. For this reason alone, a description of the design deserves its own chapter. Magnets of this type, particularly stabilized magnets, will be useful in many other experiments and the magnet built by the author for the nuclear spectrometer will undoubtedly outlive the spectrometer by many years. The descriptions in this chapter of the magnet properties and controls are intended primarily for its future users.

Magnet design

The mechanical design of the magnetic yoke is shown in figure 18. The material is hot rolled steel, no special magnetic materials have been used. The poles are 6 inches in diameter with a gap of 3-1/2 inches. This gap is reduced to 1-1/2 inches by two shaped pole caps, adjusted mechanically until they are parallel to better than .0001 inches across the diameter. The pole caps, which were carefully machined, have a rectangular ridge turned at the outside edge in order to produce a uniform field at the center of the magnet. The shape of the ridges was determined by extending the calculations of Rose (R2) to include cases where the field rises...
slightly towards the edge of the gap. With the dimensions used, the field should rise 1 part in 10,000 one inch inside the edge. The actual field is homogeneous to 1 part in 20,000 over the central two inches, but a variation of this amount may occur in a much shorter distance. The inhomogeneity results in a reduction of $T_2$ (broadening of the signals) for the narrowest signals, but the line width is narrow enough for all but the most precise measurements.

The coils consist of four one inch layers each separated by cooling coils. Each layer has approximately 800 turns of #12 Formel wire. The cooling coils are single layers of 3/16 O.D. copper tubing, five layers for each coil.

By connecting the first and last layers in series and the second and third layers in series, each coil can be split into two sections having equal resistances of 7 ohms. Thus the whole magnet can have resistances of 1 1/2, 7, or 28 ohms, depending on the connection of the four sections. The maximum current per section is 12 amps. Each section has a selenium rectifier connected backwards across it, which discharges the field very effectively when the switch is opened. The voltage reverses across the coil terminals when the current is broken, but it rises to a value less than the forward voltage.

Since uniformity is more important than high field strength, there is no choking of the magnetic circuit at the gap. The core saturates inside the coils before the pole caps are saturated. With the 1-1/2 inch gap, the field is linear
filaments of 19-6AS7's are in series and run on 115 V a-c.

MAGNET CURRENT CONTROL.

tube 6SC7.
(single cathode)

low drift input stage used in d-c amp.

fig. 19.
with current up to about 3 amps which gives 6000 gauss. 7-1/2 amps gives 10,000 gauss while the maximum current of 12 amps gives only 14,000 gauss.

Current control

The magnet is usually operated with all the coil sections in series (27 ohms), the current being controlled by a bank of 19 twin triode 6AS7's. The power is supplied by the building's motor generator sets which can deliver up to 270 volts d-c. The control circuit (figure 19) measures the magnet current by comparing the voltage developed across part of a 1 ohm potentiometer with 3 volts from dry cells. The difference is applied as a correction to the grids of the 6AS7's after an amplification of 50,000. A d-c. level control in the amplifier adjusts the current so that the difference is near zero. Since most of the disturbance comes from the motor generators, the magnet time constant should be as large as possible. The addition of a feedback path in which the a-c. voltages appearing across the magnet are fed into the control amplifier near its output restores the natural time constant of the magnet (several seconds). The amount of a-c. feedback is limited by the appearance of oscillation.

This circuit reduces the fluctuations of the magnet current to about 1 in 10,000; however, slow drifts may be several times greater. The source of the drift is variation in the heater current of the first tube of the d-c. amplifier, which is considerably improved by the use of a Miller (M2) low drift circuit.
Proton stabilizer - block diagram.

Stabilizer output

D.C. output volts.

Gauss off resonance.

Method of inserting stabilizer voltage.

PROTON STABILIZATION.

FIG 20.
Proton stabilization (P1)

The magnetic field itself is further stabilized by a control voltage derived from a proton resonance (figure 19). The proton signal is generated in an oscillating detector* which is readily tunable from 20 to 45 mc. The 500 cycle audio sweep covers a small portion of the signal which is amplified and detected by a lock-in detector similar to the one described earlier. The d-c. output of this circuit is plotted in figure 20, which shows that a field control voltage is readily available over the central region. This signal is fed into the d-c. amplifier in series with the comparison voltage.

The circuit would oscillate if the gain were not reduced greatly. This is conveniently done by throwing away voltage across a simple phase advance network (figure 20) whose use permits an increase in the maximum loop gain. Although this circuit makes the normal current control superfluous - it has been inadvertently turned off for several hours - it is still necessary if a large disturbance should throw the proton signal out of its small control range. Stabilization better than 1 part in 100,000 is achieved by use of the proton resonance.

* Older version, to be replaced by the circuit described in this thesis.
Chapter 5.
MEASUREMENTS AND STANDARDS

This chapter discusses the operation procedure for the spectrometer and the methods of computing spins, magnetic dipole moments, and electric quadrupole moments from the information it provides.

Summary of important equations

- gyromagnetic ratio \[ \gamma = \frac{\mu}{I \hbar} \]
- Larmor frequency \[ \omega_0 = \gamma H_0 \]
- maximum deflection on recording meter \[ V_{\text{max}} = \frac{1.3 \pi q N T_2^2}{b L} \frac{I(I+1)}{3kT} \gamma^2 \hbar^2 \delta \omega \]
- line width \[ \frac{1}{T_2} = \sqrt{3 \pi x} \text{(cycles between peaks)} \]
- audio sweep width \[ \delta \omega = \gamma \delta H_0 \text{ sweep current, } i \]

Choice of sample

The nuclear species in which we are interested is placed in the apparatus as a fraction of the nuclei of an element in a compound. For large signals, we require as many of the particular nuclei as possible. We also require a long relaxation time T2, but there is no point in having it longer than the limit set by the magnet. A long relaxation time is usually found in liquids or solutions containing the element, and when it is possible to use these with high concentrations,
they are used in preference to solids. For nuclei with low relative abundance, enriched samples have been used but with the exception of deuterium, these are not readily available. The size of sample used in this spectrometer is about 1 ml.

With samples having a relaxation time limited by the magnet, there is some advantage in adding a paramagnetic catalyst. Such samples have a long $T_1$ and there is considerable possibility of saturation. This applies to protons in water and may be expected for nuclei with spin 1/2 which will not have a quadrupole moment.

**Operation procedure**

Using any available spectroscopic data or theoretical predictions, the magnetic field required to bring the resonance within the range of the instrument is calculated. If this field is feasible, it is set up in the magnet and stabilized by the proton resonance. The sweep field current and the lock-in detector time constant are set at medium values and the frequency drive is turned on at its lowest speed. The spectrometer is left to hunt automatically for the resonance. It is possible to pass through resonance without detecting it. The optimum conditions for recording a wide weak line are quite different from those for a narrow strong line and, in the absence of any clue (such as a large quadrupole moment), several runs have to be taken before it can be said that the resonance is in another region or is too weak to detect.

Once the resonance is found, it can be improved by
adjusting the parameters of the spectrometer. A broad resonance allows us to increase the audio field sweep proportionally. Also, since the meter records the signal in a longer time, the time constant of the detector can be increased, reducing the bandwidth and noise. The dependence of the signal on $T_2$ can be almost removed in this readjustment.

**Measurement of frequency**

The magnetic field at the sample cannot be measured directly with the accuracy required. The measurement of the field is made by adding an internal standard such as Na whose gyromagnetic ratio is known. The measurement reduces to a comparison of the frequencies of the unknown and standard resonances. This is measured with a heterodyne frequency meter having an accuracy of at least 1 part in 10,000. The exact method of comparison has many variations. The reader is referred to methods illustrated by the measurements of Sb$^{121}$ and Cu$^{63}$ given in the next chapter.

**Calculation of spin**

Values for the spin of most nuclei are available from spectroscopic and other measurements. Where the spin is in doubt, it can be checked from the observed maximum meter deflections, line widths, and audio sweep currents for the unknown and standard signals. We can eliminate all factors common to the two resonances and obtain

$$I_x(I_x + 1) = \frac{N_s}{N_x} \left(\frac{W_x}{W_s}\right)^2 \left(\frac{\nu_x}{\nu_s}\right)^3 \frac{V_x}{V_s} \frac{i_s}{i_x} I_s(I_s + 1)$$

where $W$ is the distance between the peaks and $i$ is the sweep
current. \( x \) refers to the unknown and \( s \) to the standard. In this measurement, one must be careful that the conditions of small sweep and no saturation still pertain.

**Calculation of magnetic dipole moments**

We have from our apparatus the ratio of the resonant frequencies of the unknown and the standard. Using published values, it is a simple matter to arrive at the ratio of the resonant frequency of the unknown in our sample to the proton in water. This should be the ratio of the gyromagnetic ratios and from the known value of the proton moment, we can calculate the magnetic moment of the unknown.

The proton moment is known from two separate methods, molecular beam measurements with considerable correction, and measurements at the National Bureau of Standards of proton resonances in a magnet calibrated by the force on a conductor carrying a known current (T1). These agree very well and the best value at present is \( 2.7935 \pm 0.0004 \) nuclear magnetons (P3).

The simple calculation outlined above is probably quite safe for accuracies of a one part in a thousand, but it assumes that the fields at the nuclei are not disturbed by the atomic electrons. For free atoms, there is an internal diamagnetism arising in the electrons. The magnitude has been calculated by Lamb (L1) who finds a correction of

\[
0.319 \frac{Z^4}{3}
\]

must be applied. This correction is applied so that it increases the calculated magnetic moment. Since uncorrected frequency ratios are usually quoted, this correction is applied
in the last step only.

We are still assuming that every compound, at least in solution, will give the same resonant frequency. Recently, Proctor (P12) and Dickinson (D2) have shown that this is not true. Proctor's illustration is most striking. A solution of NH$_4$NO$_3$ gives two N$^{14}$ resonances several kilocycles apart. Presumably one arises in the NH$_4$ ion and the other in NO$_3$. A similar effect discovered by the author for Sb$^{121}$ will be discussed in the next chapter. If this difference arises from the diamagnetism of the molecular electrons, it is difficult if not impossible to calculate. The lack of central symmetry in many molecules and ions further complicates the problem. Indeed, this author feels that the differences observed will be utilized as an aid in the determination of molecular structure rather than the use of molecular structure to determine the true magnetic moment. These discoveries show that much of the extreme accuracy quoted in the literature for frequency ratios is of dubious value, particularly where the exact constitution of the sample is not given.

These considerations also apply to the internal standard used. It is hoped that similar work will be done on sodium compounds since it has been widely used as a standard. No differences have been found for proton signals in a wide variety of samples and the precise measurements of the very light nuclei must still be accepted. Frequency comparisons directly with proton signals have only the possible error in the "unknown" resonance.
Calculation of quadrupole moments

Pound has calculated a few quadrupole moments by comparing line widths for nuclei with known and unknown quadrupole moments (P5), (P6). If Q is the only cause, the relaxation time $1/T_2$ should vary as $Q^2$, where Q is the quadrupole moment in cm$^2$, and as the electric field gradient. The latter may be neglected when both nuclei are the same element, but when they differ, Pound calculates the ratio of the two gradients using ionic radii. The author's own work (next chapter) throws some doubt upon these calculations, and more experimental and theoretical work is necessary before reliable Q's can be obtained from nuclear induction measurements.
FIGURE 21.

to face page 45
Chapter 6.

RESULTS

The nuclear spectrometer has been in operation for only a few weeks. Some results of significance have been obtained already and are reported in this chapter. It is intended to exploit the excellent performance of this spectrometer in the immediate future by extending the measurements to other nuclear species.

Cu$^{63}$ from copper in the driving coil

Weak signals apparently arising from the metallic copper in the wire of the driving coil were first reported by Pound. We have found signals which have been identified as arising from this source (figure 21). The frequency ratio to sodium was carefully measured because the resonance was not immediately identified as Cu$^{63}$. The results are summarized here since they constitute a demonstration of the reliability of the frequency measurements.

The sample contained a small amount of NaCl, which gave sodium resonances very close to the coil resonance. The following method was used to find the frequency ratio:

(a) The frequency was swept slowly down through the Cu resonance. After this was complete, the gain, detector time constant, and audio sweep were reduced so the Na signal
would be clearly recorded. The frequency of the Na signal was observed by noting zero beat on the heterodyne frequency meter as the recording meter passed through zero. This procedure was repeated five times.

(b) The rate of sweep in the region of the signals was obtained by sweeping the frequency over the same range and marking zero beats for a series of settings of the frequency meter.

(c) The Cu frequency was calculated by adding the small measured differences to the Na frequency.

The whole procedure was repeated by rotating the tuning condenser 180° and sweeping the frequency up through the Na and then the Cu resonances. Since rather long time constants were used, the recording meter needle may have lagged behind the true reading. This effect will cancel out by averaging the two sets of meter readings.

The least squares solution for the rate of sweep with decreasing frequency was 19.9 kc/inch, with a paper speed of 6"/hr. The average of the five tracings gives \( V_{\text{Cu}^{63}/\text{Na}^{23}} = 1.00425 \pm 0.00005 \). Similar measurements with increasing frequency gives \( V_{\text{Cu}^{63}/\text{Na}^{23}} = 1.00402 \pm 0.00004 \). The difference between the two groups of readings is real and can be attributed to the long time constant for the Cu traces.

The average of the two groups is 1.00413 \( \pm \) 0.00006. The precision does not take into account systematic errors. An asymmetry is easily visible in the traces (figure 21) which forced the author to reduce the precision considerably. A
reliable estimate gives \( \nu \text{Cu}_6/\nu \text{Na}_3 = 1.0041 \pm 0.0003 \).

This value is not in agreement with the results of measurements on a cuprous salt. Bitter's values (B2) give for this ratio \( \nu \text{Cu}_6/\nu \text{Na}_3 = 1.0021 \pm 0.0002 \). However, after it was known that the signals came from the coil, the value was checked against the work of Knight (K1). He compared the frequency of Cu\(_6\) in finely powdered metallic copper and in cuprous chloride, and found the metallic resonance to be 23.7 kc higher than the resonance from the salt which was at 10.123 mc. Using these values, we calculate \( \nu \text{Cu}_6/\nu \text{Na}_3 = 1.0044 \pm 0.0002 \) for metallic copper. Our result is in good agreement with this value.

Knight also publishes a tracing of the copper signals which may be compared with figure 21. The signal to noise ratio is about the same, although he had much more copper effectively in the r-f field.

Knowing the origin of the signal, it is possible to explain the asymmetry noted above. The field \( H_1 \) penetrates only a short distance into the copper wire and is shifted in phase from the field in free space. We are thus detecting a mixture of absorption and dispersion giving a distorted signal.

**Magnetic moment of Sb\(_{121}\)**

Sb\(_{121}\) resonances have been recorded with samples of H\(\text{SbCl}_6\) and \(\text{SbCl}_5\). The \(\text{SbCl}_5\), which is a fuming liquid, was used directly from the re-agent bottle. The \(\text{H}\text{SbCl}_6\) was prepared by adding the \(\text{SbCl}_5\) to concentrated hydrochloric acid in approximately equal amounts. Reproductions of the traces are
are given in figure 22. No signals were found with an HCl solution of SbCl₃.

Measurements were taken by placing one test-tube each of HSbCl₆, SbCl₅, and saturated solution of NaBr in the coil of the oscillating detector one after the other. The center of each resonance was measured by the heterodyne frequency meter as the recording meter needle crossed the zero line. The large signals made this spot measurement possible, but the accuracy depends on the stability of the magnet proton control. The measurements were repeated three times. The frequencies quoted below are twice the actual value, because the frequency meter was measuring the 2nd harmonic of the oscillator.

<table>
<thead>
<tr>
<th></th>
<th>1st run</th>
<th>2nd run</th>
<th>3rd run</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na²³ in NaBr</td>
<td>15.084</td>
<td>15.084</td>
<td>15.084</td>
</tr>
<tr>
<td>Sb¹²¹ HSbCl₆</td>
<td>13.648</td>
<td>13.648</td>
<td>13.648</td>
</tr>
<tr>
<td>Sb¹²¹ SbCl₅</td>
<td>13.657</td>
<td>13.657</td>
<td>13.656</td>
</tr>
<tr>
<td>ratio HSbCl₆</td>
<td>.9048</td>
<td>.9048</td>
<td>.9048</td>
</tr>
<tr>
<td>ratio SbCl₅</td>
<td>.9054</td>
<td>.9054</td>
<td>.9053</td>
</tr>
</tbody>
</table>

Shifting the position of the NaBr sample in the coil gave a difference of less than 1/2 in the last place.

The values are: $\nu_{Sb^{121}/Na^{23}} = .9048 \pm .0001$ for a sample of HSbCl₆. This confirms exactly a value obtained by Proctor (private communication)¹: $\nu_{Sb^{121}/Na^{23}} = .9054 \pm .0002$ for a sample of SbCl₅. The difference is quite large, but the almost exact repetition of the resonant frequencies indicates that it is real. This is a further example of the

¹The author is indebted to Professor Bloch for this information.
chemical shift found for fluorine and nitrogen isotopes by Dickinson (D2) and Proctor (P12). If the ratio is rounded off to .905, the value for the magnetic moment becomes 3.36 nuclear magnetons which is to be compared with the spectroscopic value obtained by Crawford (C3) of 3.7 nuclear magnetons.

**Line widths of bromine and iodine isotopes**

Pound has reported resonances observed for I\(^{127}\), Br\(^{79}\), and Br\(^{81}\) (P5) (P6). He found the iodine resonance to be 14 kc. wide and the two bromine resonances to be 10 kc. wide, Br\(^{79}\) being slightly wider than Br\(^{81}\). Iodine is known to have a large quadrupole moment and, assuming the line widths to arise only from quadrupole coupling, Pound calculated the quadrupole moment of bromine by comparing the resonance widths. The electric field gradient is assumed to arise from the water molecules and Pound allowed for the greater distance of the iodine nuclei from the electric dipoles in the water molecules. These calculations give a value for the quadrupole moment of bromine which has been verified by microwave spectroscopy (G1).

The author has recorded resonances for these isotopes using saturated aqueous solutions of NaI, KI, NaBr, KBr. Some of the traces are reproduced in figure 23. This figure shows clearly that there is a marked discrepancy for Br\(^{81}\) width in NaBr solution, but the iodine width in NaI is approximately in agreement with Pound's value. Widths measured on tracings taken with a higher paper speed are:
The bromine isotopes have slightly narrower resonances in KBr solution. Of more interest is the width of about 2 kc for I$^{127}$ in KI (figure 23). If Pound's assumptions are correct, one would expect the width to be the same order as found for NaI solution.

A further peculiarity of the bromide solutions is the extreme sensitivity of the bromine resonances to the addition of the paramagnetic salt MnCl$_2$.4H$_2$O. The addition of a minute crystal to samples of KBr and NaBr caused a marked reduction in the relaxation time. The salt was added to the sample as it sat in the apparatus, and tracings were taken without varying any parameters. The amplitude of the signal for Br$^{81}$ in KBr was reduced by a factor of four, and the line width increased by a factor of two. This is consistent with a reduction of T$_2$ by a factor of two. The concentration of the paramagnetic salt was of the order of .001 M. Similar results were obtained using NaBr solution, but the sodium resonance was not affected.

It is difficult to imagine any experimental error which would make the bromine signals ten times too narrow. The conclusion appears to be that quadrupole moments cannot be reliably estimated from nuclear magnetic resonance without
further experimental and theoretical work.
APPENDIX I.

An Estimation of Noise in a Van der Pol Oscillator

The noise appearing as an audio modulation of a van der Pol oscillator can be approximately calculated simply in the following manner. It is assumed that the noise arising in the tuned circuit can be separated into Fourier components in the usual way. The response of the circuit to these r-f. frequencies will be calculated using equations provided by van der Pol (V2) and treating each component independently. The resultant noise amplitudes will be detected by a linear detector and the audio noise (20 to several thousand cycles) calculated. Where it is necessary to insert values for approximation, those found for the circuit described in chapter 3 of this thesis will be used.

To set up the differential equation, we consider the triode circuit used in chapter 2, with the addition of a noise current

$$
\overline{i^2} = \frac{4kT \Delta \nu}{R}
$$

flowing into the tuned circuit whose parallel resistance is R (figure 24).

The current equation gives

$$
C \frac{dv}{dt} + \left[ \frac{v}{R} - \frac{M}{L} \frac{dv}{dt} \right] + \frac{1}{L} \int v dt = - \left( \frac{4kT \Delta \nu}{R} \right)^{\nu_2} \cos \omega t \quad (1)
$$

or

$$
\frac{d^2 v}{dt^2} + \frac{dv}{dt} \left[ \frac{1}{C} \left( \frac{1}{R} - \alpha \right) \gamma + \frac{\beta^2 v^2 + \delta \nu^3}{C} \right] + \frac{v}{LC} = \frac{\omega}{RC} \left( \frac{4kT \Delta \nu}{R} \right)^{\nu_2} \sin \omega t \quad (2)
$$
We are now ready to apply van der Pol's solution for the problem of forced oscillation. He starts with the differential equation
\[ \frac{d^2 v}{dt^2} - \frac{1}{C} \left( \frac{d}{dt} (\alpha' v - \gamma' v^3) + \omega^2 v \right) = \omega^2 E \sin \omega t \] (3)
which can be found on page 1068 of his article [V2].

Comparison with our equation shows that
\[ \alpha' = \frac{1}{C} (\alpha - \frac{1}{R}) \]
\[ \gamma' = \frac{1}{C} \gamma \]
\[ E = \frac{1}{\omega^2 RC} \left( 4kT R \Delta V \right)^{1/2} \]
\[ \beta' = \frac{\beta}{C} = 0 \] (characteristic of van der Pol oscillator).

We now quote results from his paper and modify them to our purpose. So that comparison with the original work will be direct, we shall drop the primes in the constants just listed and shall continue for the present in the nomenclature used in the relevant section of van der Pol's paper.

He finds the concepts of free and forced oscillations have lost their rigorous meaning, but he defines \( a \) as the amplitude of oscillation with frequency \( \omega_0 \) ("free"), and \( b \) as the amplitude of oscillation of frequency \( \omega_1 \) ("forced"). Both these frequencies can exist simultaneously, and he finds
\[ a^2 = a_o^2 - 2b^2 \] (5)
\[ b^2 \left\{ \frac{2}{\omega_1^2} + a^2 (1 - \frac{3b^2}{a_o^2}) \right\} = \omega_1^2 E^2 \] (6)
where \[ a_o = \sqrt{\frac{2}{\gamma} \frac{1}{\alpha}} \] is the amplitude of the oscillation in the absence of a forcing voltage, and \( \varepsilon = 2(\omega_1 - \omega) \).
Equation 5 shows that when \( b^2 > \frac{1}{2} a_0^2 \) the amplitude of the free oscillation is completely suppressed. Van der Pol finds for the case where \( a \) is zero

\[
b^2 \left\{ \frac{z^2}{\omega_0^2} + \alpha^2 \left( 1 - \frac{b^2}{a_0^2} \right) \right\} = \omega_1^2 E^2
\]

Equations 6 and 7 are cubic in \( b^2 \) and give three real positive solutions when \( z/\alpha \) is near zero. The larger value of \( b^2 \) is the stable one and if \( E \) is small \( b^2/a_0^2 \) is slightly greater than unity. In this region, the free oscillation is completely suppressed, a condition often found in practice and known as "locking." Using the approximation \( b^2/a_0^2 \approx 1 \), it can be shown that the width of the region of three solutions is

\[
\left( \frac{z}{\alpha} \right)^2 = \frac{3}{2} \left( \frac{\omega_1 E}{\alpha a_0} \right)^2 \quad \text{for equation (6)}
\]

\[
\left( \frac{z}{\alpha} \right)^2 = \frac{1}{2} \left( \frac{\omega_1 E}{\alpha a_0} \right)^2 \quad \text{for equation (7)}
\]

The two solutions obtained by van der Pol do not agree upon the extent of the region of locking with small driving voltages. Substitution of numerical values for our oscillator into equations 8 and 9 shows that the width of this region is much less than one cycle for noise e.m.f.'s, and we are only interested in those r-f. frequencies which differ from \( \omega_0 \) by more than 20 cycles.

For these frequencies with small \( E \), equation 6 is applicable and it has only one solution for \( b^2/a_0^2 \) which is much less than unity.

We can simplify the equation to

\[
b^2 (z^2 + \alpha^2) = \omega_1^2 E^2
\]
A further simplification results from our upper audio limit. \( \alpha \) as here defined is about \( 4 \times 10^4 \) cycles when our oscillator is operating at 1 volt r-f. \( \alpha^2 \) is much larger than \( z^2 \) for \( z \) in the audio range and (10) becomes

\[
b^2 = \frac{\omega^2 E^2}{\alpha^2} \quad \text{and remembering} \quad a_0^2 = \frac{\alpha}{\gamma}.
\]

We now revert to our original nomenclature. Equation (11) becomes

\[
b^2 = \frac{\omega^2 E^2}{\left(\frac{3}{4} \gamma a_0^2\right)^2}
\]

This is the amplitude of r-f. noise components in the oscillator, which differ from the oscillator frequency by an audio frequency. These frequencies on each side of the central frequency will appear as an audio modulation after detection. Because of the presence of the large central frequency voltage, the side bands simply add quadratically and cross products are negligible. The audio noise as a modulation is

\[
\mu_n^2 = \frac{8 k T R \Delta V}{\left(\frac{3}{4} \gamma V^2 R\right)^2}
\]

No allowance has been made for noise originating in the tubes themselves. It is probable that this can be done by introducing the noise factor \( F \) for the tubes used as an amplifier.

\[
F = \frac{\text{noise power from input circuit} + \text{amplifier}}{\text{noise power from input circuit alone}}
\]

\( F \) is dependent upon the frequency and the impedance of the input circuit (VI). For a given tube type, \( F \) has a minimum value which lies between 1 and 2 for the less noisy tube types. The equations above are modified by replacing \( R \) by \( FR \)
wherever we are concerned with the generation of noise.

\[
\overline{\nu_n^2} = \frac{8kTFR\Delta\nu}{\left(\frac{3}{4}ky\nu^2R\right)^2}
\]

(14)

It is appreciated that the assumption of independence of noise components when applied to a non-linear tube is not strictly correct. However, the transconductance at any instant is almost completely determined by the large oscillating voltage; the small noise voltages produce very little change. This situation is similar to the well-known problem of the detection of signals in the presence of a large voltage of central frequency; as already noted, cross-modulation products do not appear. The author feels that equation 14 must represent closely the modulation noise of a van der Pol oscillator.
APPENDIX II.

A Table of Nuclear Magnetic Resonances

This table contains values for the ratio of resonant frequencies to the frequency of the proton. No diamagnetic correction is included. This table contains only those nuclei which have been measured by paramagnetic resonance methods, and only one reference is given for each nucleus; for further information, refer to the tables of Chambers and Williams (C2), and Poss (P3).

\[
\begin{align*}
\nu_{\text{He}}/\nu_{\text{H}} & = .685001 \pm .000030 \quad (B8) \\
\nu_{\text{Be}}/\nu_{\text{H}} & = .1535063 \pm .000002 \quad (B7) \\
\nu_{\text{B}}/\nu_{\text{H}} & = 1.066636 \pm .000010 \quad (B4) \\
\nu_{\text{He}}/\nu_{\text{He}} & = .7617866 \pm .0000012 \quad (A2)
\end{align*}
\]

The accuracy quoted for many nuclei in the remaining part of the table is justified only for the particular sample used in the measurement (P12), (D2). Since the exact constitution of the sample is rarely given, accuracy greater than \(1\) part in a few thousand is suspect.

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>(\nu/\nu_{\text{H}})</th>
<th>Error (\times 10^{-5})</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li7</td>
<td>.388625</td>
<td>4.0</td>
<td>(B2)</td>
</tr>
<tr>
<td>Be9</td>
<td>.1405187</td>
<td>.02</td>
<td>(D3)</td>
</tr>
<tr>
<td>B10</td>
<td>.10745</td>
<td>11</td>
<td>(B2)</td>
</tr>
<tr>
<td>B11</td>
<td>.320827</td>
<td>.04</td>
<td>(A1)</td>
</tr>
<tr>
<td>Cl3</td>
<td>.25143</td>
<td>5</td>
<td>(P2)</td>
</tr>
<tr>
<td>Nucleus</td>
<td>$v/v_{\text{H}1}$</td>
<td>Error x 10^{-5}</td>
<td>Ref.</td>
</tr>
<tr>
<td>---------</td>
<td>------------------</td>
<td>------------------</td>
<td>------</td>
</tr>
<tr>
<td>N$^{14}$</td>
<td>0.072255</td>
<td>0.8</td>
<td>(P11)</td>
</tr>
<tr>
<td>N$^{15}$</td>
<td>0.10132</td>
<td>1</td>
<td>(P11)</td>
</tr>
<tr>
<td>P$^{19}$</td>
<td>0.94077</td>
<td>10</td>
<td>(P2)</td>
</tr>
<tr>
<td>Na$^{23}$</td>
<td>0.26450</td>
<td>3</td>
<td>(B2)</td>
</tr>
<tr>
<td>Al$^{27}$</td>
<td>0.26056</td>
<td>3</td>
<td>(B2)</td>
</tr>
<tr>
<td>P$^{31}$</td>
<td>0.40481</td>
<td>4</td>
<td>(B2)</td>
</tr>
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<td>Cl$^{35}$</td>
<td>0.09799</td>
<td>7</td>
<td>(C1)</td>
</tr>
<tr>
<td>Cl$^{37}$</td>
<td>0.11773</td>
<td>8</td>
<td>(P11)</td>
</tr>
<tr>
<td>V$^{51}$</td>
<td>0.26290</td>
<td></td>
<td>(K2)</td>
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<td>Mn$^{55}$</td>
<td>0.24789</td>
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</tr>
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<td>Co$^{59}$</td>
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<td>Cu$^{63}$</td>
<td>0.26506</td>
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<td>Ga$^{71}$</td>
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</tr>
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<td>Br$^{81}$</td>
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</tr>
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</tr>
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<td>(P10)</td>
</tr>
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</tr>
<tr>
<td>Sn$^{119}$</td>
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<td>14</td>
<td>(P9)</td>
</tr>
<tr>
<td>Nucleus</td>
<td>$\nu / \mu_1$</td>
<td>Error $\times 10^{-5}$</td>
<td>Ref.</td>
</tr>
<tr>
<td>---------</td>
<td>---------------</td>
<td>-------------------------</td>
<td>----------------</td>
</tr>
<tr>
<td>Sb$^{121}$</td>
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<td>20</td>
<td>(this thesis)</td>
</tr>
<tr>
<td>Tl$^{127}$</td>
<td>0.20003</td>
<td>7</td>
<td>(Z1)</td>
</tr>
<tr>
<td>Cs$^{133}$</td>
<td>0.13093</td>
<td>14</td>
<td>(Cl)</td>
</tr>
<tr>
<td>La$^{139}$</td>
<td>0.141251</td>
<td>1.4</td>
<td>(D1)</td>
</tr>
<tr>
<td>Pt$^{195}$</td>
<td>0.21496</td>
<td>4</td>
<td>(P10)</td>
</tr>
<tr>
<td>Hg$^{199}$</td>
<td>0.17879</td>
<td>2</td>
<td>(P10)</td>
</tr>
<tr>
<td>Tl$^{203}$</td>
<td>0.571499</td>
<td>5</td>
<td>(P2)</td>
</tr>
<tr>
<td>Tl$^{205}$</td>
<td>0.577135</td>
<td>5</td>
<td>(P2)</td>
</tr>
<tr>
<td>Pb$^{207}$</td>
<td>0.20898</td>
<td>6</td>
<td>(P9)</td>
</tr>
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</table>
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