A THEORETICAL INVESTIGATION OF THE NUCLEAR RESONANCE SPECTRUM OF $^{11}\text{B}$ IN KERNITE

by

JAYASEETHA NITTOOR SREENIVASA RAU

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We accept this thesis as conforming to the standard required from candidates for the degree of MASTER OF SCIENCE

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ABSTRACT

In this thesis a theoretical study is made of the resonance spectra of the B\textsuperscript{11} nuclei in a single crystal of Kernite (Na\textsubscript{2}B\textsubscript{4}O\textsubscript{7}.4H\textsubscript{2}O) whose quadrupole moments interact with the electric field gradient at the nuclear sites in the crystal in the presence of an external magnetic field when the magnetic and quadrupole interaction energies are comparable.

Using the results of the high field work of Waterman and Volkoff, energy levels and transition frequencies have been calculated numerically using the University of British Columbia ALWAC-III-E digital computer over a range of magnetic fields in the region intermediate between the limiting cases of pure quadrupole energy levels slightly perturbed by magnetic interactions and Zeeman energy levels slightly perturbed by quadrupole interactions. The magnetic field was taken to be oriented in the plane perpendicular to the two-fold symmetry axis of the crystal and the calculations were carried out for different orientations of the external magnetic field in steps of 30°.

A general theory has been developed for the calculation of signal intensities in the case of crossed coil spectrometer (induction method) and has been applied to the present case.

The signal intensities for absorption type spectrometers are proportional to the transition probabilities, and results are given for the case of Kernite which enables one to compare the expected signal intensities of absorption spectrometers with those of induction spectrometers.
In presenting this thesis in partial fulfilment of the requirements for an advanced degree at the University of British Columbia, I agree that the Library shall make it freely available for reference and study. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by the Head of my Department or by his representative. It is understood that copying or publication of this thesis for financial gain shall not be allowed without my written permission.

Department of Physics

The University of British Columbia, Vancouver B, Canada.

Date 12th July, 1958
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<td>along the z principal axis</td>
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I would like to express my sincere thanks to Dr. G.M. Volkoff for suggesting the problem and I am indebted to Dr. M. Bloom for guiding this research and for taking a constant interest in the work.

This work was made possible by the use of the electronic computer at the University of British Columbia. I gratefully acknowledge the assistance and cooperation given by the staff of the computing centre. I should like to thank Dr. J. M. Daniels and Mr. J.R.H. Dempster for acquainting me with programming.

Finally I would like to thank the members of the Department who through lectures and discussions have increased my knowledge of physics.
CHAPTER 1

INTRODUCTION

The properties of angular momentum and magnetic moment were first ascribed to the nucleus by Pauli (1924) in order to account for the hyperfine structure of atomic spectra.

A magnetic dipole experiences a force when placed in an inhomogeneous magnetic field. Atoms or molecules which possess a magnetic moment are therefore deflected on passing through such a field. This technique was used with great success in the classic atomic beam experiments of Stern and Gerlach to prove experimentally that the measurable values of the components of an atomic magnetic moment do not take on a continuous range of values; instead they form a discrete set corresponding to the space quantization of the atom in the magnetic field. From the magnitude of the deflection of the beam the atomic magnetic moment can be evaluated.

The beam method was powerfully improved by Rabi and his colleagues by the introduction of the resonance method. In addition to the steady magnetic field, the molecules of the beam are subjected to electromagnetic radiation of such a frequency as to induce transitions between their quantized energy levels by a process of absorption or stimulated emission of quanta of energy. If the nuclear spin is $I$, each energy level is split by the steady magnetic field into $2I + 1$ equally spaced sub levels. If the
maximum measurable component of the nuclear magnetic moment is $\mu$, the separation between the lowest and the highest sub levels is $2\hbar H$ in a steady magnetic field $H$. The separation between successive sub levels is $\hbar H/l$. The frequency of the electromagnetic radiation whose quanta can excite transitions between these sub levels is thus equal to $\omega_H/l$. The frequency of this resonant exchange of energy in a given field is found experimentally by the sharp reduction in the number of molecules reaching the detector.

The resonant exchange of energy between the $2I + 1$ energy levels of a nuclear magnetic moment in a magnetic field is not restricted to matter in the form of molecular beams, but also occurs in ordinary solids, liquids or gases.

The first successful nuclear magnetic resonance experiments using bulk material were carried out independently at the end of 1945 by two groups. Bloch, Hansen and Packard (1) measured induction signals from transitions between proton levels in water, while Purcell, Torrey and Pound (2) detected the absorption of energy from a resonant electronic circuit by proton transitions in paraffin wax.

Nuclei of spin $I$ greater than $1/2$ possess electric quadrupole moments. The quadrupole moment is a measure of the departure of the nuclear charge distribution from spherical symmetry. Deviations from an interval rule in the spectrum of Europium, observed in 1935 were explained by Casimir (3), who suggested that the nucleus had a non-spherical charge distribution which would lead to a quadrupole moment. The interaction energy
of the nucleus with the electrostatic field gradient produced by
the surrounding electron cloud is different for different
orientations of the nucleus.

In many substances (e.g. cubic crystals) the
electrostatic field gradient averages out to zero, so that the
quadrupole effect can be neglected so far as the energy levels
are concerned. However, in the case of some molecules, and in
many crystals, it is possible for a nucleus to be placed at a
position where the electrostatic field gradient does not average
to zero, and the resulting interaction will change the energy
levels of the nucleus.

In 1948 Bloembergen (4) reported effects of quadrupole
interactions with the deuteron. Pound (5) found nuclear magnetic
resonances which were split into several lines by the quadrupole
interaction in single crystal. In 1951 Dehmelt and Kruger (6)
found resonance due to transitions between nuclear quadrupole
energy levels, using the techniques of nuclear magnetic resonance
but with no applied magnetic field.

If we subject a crystal in which there is an electric
quadrupole interaction to an external magnetic field, the Zeeman
levels will be perturbed, and the single Zeeman line will be split
into many components.

At one extreme we have the case where the magnetic
interaction of each dipole with an external magnetic field
produces Zeeman levels separated by energies quite large compared
to the splitting due to quadrupole interaction of the nucleus with
its surroundings. In these instances, the quadrupole interaction is taken as a perturbation on the Zeeman effect. Carr and Kikuchi (7) have obtained an expression for the transition frequencies to the first order in the ratio \( \frac{eQ\phi z z}{\gamma Ho} \). Pound (5) extended it to the third order in case of axially symmetric field, and this theory has been further extended to the case of asymmetric field gradients by Bersohn (8) and Volkoff et al (9).

At the other extreme, Dehmelt and Kruger (10) have investigated theoretically and experimentally the pure quadrupole case and have obtained information on the quadrupole coupling constant in case of axially symmetric crystals. The theory was then extended to non symmetric crystalline field gradient by Kruger (11) in which case the splittings depend on both the quadrupole coupling constant and the degree of asymmetry of the field. Bersohn (13) gives a general expression for the perturbation in terms of an axial asymmetry parameter up to the fourth order.

The introduction of a weak external magnetic field can be treated as a perturbation on the pure quadrupole levels. Kruger (11) obtained a first order expansion in terms of the magnetic field strength.

As the external magnetic field is increased the perturbation theory breaks down where the quadrupole interaction energy is comparable with magnetic interaction. Experimental investigations on Kernite have been made at the two extreme cases discussed above. Waterman and Volkoff (13) have investigated the resonance absorption spectrum of \(^{11}B\) nuclei in a single crystal.
of Kernite (Na$_2$B$_4$O$_7$, 4H$_2$O) placed in a large uniform external magnetic field and have discussed their result in terms of perturbation of the nuclear Zeeman energy levels by the interaction of the nuclear electric quadrupole moment with the crystalline electrostatic field gradient. It was necessary to go to second order perturbation theory to get agreement with experiment. The work of Hearing and Volkoff (14) gives information about the resonance absorption spectrum of the same nuclei in terms of perturbation of the nuclear electric quadrupole energy levels by the magnetic interaction. Not all the experimental results at low field are consistent with the high field experiment.

The present calculations have been carried out along the same lines as has been done previously for the case of Spodumene (15 and 16) in which case the two extreme regions are linked together and a complete knowledge of the energy levels, the frequencies and intensities of transitions are obtained by a direct numerical solution of the secular determinant. The above work on Spodumene represents the first system in which the nuclear resonance spectrum extending from the low field to the high field region through the region of intermediate fields has been studied completely both theoretically and experimentally. There was complete agreement of the experimental values of the transition frequencies with the theoretical calculations. The signal intensities will be discussed below.

In this thesis we calculate the energy levels and transition frequencies for B$^{11}$ in Kernite over an intermediate range of values of magnetic field showing the gradual transition
from a pure quadrupole spectrum to the other extreme of a single Zeeman line split into a number of closely spaced components.

In addition, calculations have been done to predict relative signal intensities as the magnetic field is varied for both absorption and induction (e.g. crossed coil) types of spectrometers. That the two types of spectrometers should measure different relative signal intensities as a function of field in systems involving quadrupole interactions arose out of Robinson's experiments on Spodumene, mentioned above, which were done using a crossed coil spectrometer. A theory has been developed to explain Robinson's results on intensities (15, 17). In Chapter V, a generalization of this theory has been developed, which is applicable to the case of Kernite. It is felt that these calculations will aid the experimenter in choosing the type of spectrometer suitable for investigating the $^{11}B$ spectrum in Kernite.

In Chapter II of this thesis the crystal structure of Kernite and the high field results of Waterman and Volkoff are discussed. We discuss in Chapter III the Hamiltonian to be diagonalized in order to calculate energy levels of $^{11}B$ nuclei in Kernite, while the results of numerical calculations are given in Chapter IV.
CHAPTER II

INFORMATION ON KERNITE

(a) Crystallographic

The Kernite Crystal, Na₂B₄O₇.4H₂O is monoclinic and contains four formula units, and therefore sixteen B¹¹ nuclei per unit cell. X-ray studies (18) give the information that starting with one formula unit a second may be obtained by inversion in a symmetry centre, while the other two may be obtained from the first two by a rotation about a two-fold symmetry X crystal axis. Inversion in a symmetry centre guarantees that the sixteen B¹¹ sites consist of eight pairs, the members of each pair having electric field gradient tensors identical both in orientation and magnitude.* The existence of a twofold symmetry axis further guarantees that the eight pairs break up into four groups of two pairs each. One pair of each group may differ from the other pair of the same group only by the orientation of the principal axes of the electric field gradient tensors, which are symmetrically inclined with respect to the twofold rotation axis of the crystal. Thus among the sixteen boron sites in a unit cell we may expect to find at most four numerically different field gradient tensors, with each of these tensors repeated in a possibly different orientation. If the crystal symmetry axis is held either

* A more precise description of the electric field gradient tensor is postponed until Chapter III.
Figure 1: A three dimensional model of the unit cell of Kernite ($\text{Na}_2\text{B}_4\text{O}_7$, $4\text{H}_2\text{O}$). The brown balls are boron, the white are oxygen, the yellow are sodium and the blue are water. The symmetry axis is vertical.
perpendicular or parallel to the magnetic field the two
symmetrically inclined tensors are equivalent, and there are
at most only four non-equivalent $B_{11}$ sites. For all other
orientations of the crystal there may be eight non-equivalent
$B_{11}$ sites, provided none of the tensor axes are parallel to
the symmetry axis of the crystal. Because of the experimental
simplification resulting from suitable choice of magnetic field
directions as described above, the calculations reported in this
thesis are confined to orientations of the external magnetic
field in the plane perpendicular to the $X$ symmetry axis (the
YZ plane).

Figure 1 shows a photograph of a model of the Kernite
unit cell.

(b) **High field results**

The work of H.H. Waterman and Volkoff (13) at this
laboratory has given a complete analysis of the quadrupole
coupling tensors for $B_{11}$ nuclei in Kernite. The above work
was an extension of the study of nuclear resonance absorption
spectra of single crystals in high external magnetic fields,
insofar as it treats a spectrum complicated by the existence
of non-equivalent sites for nuclei of the same species. In
addition to leading to information regarding the orientation
of the principal axes of the electric field gradient tensors
relative to the crystallographic axes, a study of the dependence
on crystal orientation in the external magnetic field of the
Zeeman resonances perturbed by the quadrupole interaction of
the nuclei, gives the value of the quadrupole coupling constant
and of the asymmetry parameter which characterise the quadrupole Hamiltonian. These quantitative results of Waterman and Volkoff (13) are tabulated in the next section and these results form the starting point of the present investigation.

It was found from the experiments of H.H. Waterman on Kernite that two of the four non-equivalent $^{11}$B sites which are designated by C and D have smaller quadrupole coupling constants and first order perturbation theory is good enough for these sites. On the other hand for the other two sites which are referred to as E and P, the electric quadrupole perturbation is strong enough to require second order effects to be considered. The sites referred to as C and D by Waterman and Volkoff will not be further discussed here. We shall be interested in calculations of energy levels and transition frequencies for the E and P sites in a region of magnetic field strengths in which perturbation theory is not applicable. Over a large part of this region second order perturbation theory would be adequate to calculate transition frequencies for C and D sites.

* These remarks pertain to external magnetic fields of the order of 7000 gauss or higher.
CHAPTER III

GENERAL HAMILTONIAN AND THE CASE OF KERNITE

The Hamiltonian describing the interaction between the nuclear electric quadrupole moment $Q$ and the electric field gradient at the nuclear site, and the interaction between the nuclear magnetic moment $\mu$ and an externally applied magnetic field $H_0$, most conveniently expressed for our purposes in the principal axis coordinate system of the electric field gradient, is given by (13).

$$\hat{H} = \frac{e\phi_{zz}}{4I(2I-1)} \left[ (3I_z^2 - I^2) + (I_x^2 - I_y^2) \eta \right] - \frac{\mu H_0}{I} \left[ aI_x + bI_y + cI_z \right] \tag{1}$$

where $x, y, z$ are the principal axes of $\phi_{ij} = \frac{\partial^2 \phi}{\partial x_i \partial x_j}$, where $\phi$ is the electrostatic potential at the nuclear site, $I_x$, $I_y$ and $I_z$ are the component of the nuclear spin operator $I$, $\eta$ is the asymmetry parameter

$$\eta = \frac{(\phi_{xx} - \phi_{yy})}{\phi_{zz}}$$

and $a, b, c$ are the direction cosines of $H_0$ relative to the principal axes of the electric field gradient tensor.

If we set $I = \frac{3}{2}$ for $B^{11}$, and divide (1) by $e\phi_{zz}$ then, in the representation in which $I_z$ is diagonal, the Hamiltonian matrix to be diagonalized is of the following form
Since we are interested here in a numerical calculation for a specific system, we shall express the above quantities in terms of parameters convenient for the study of the Kernite system.

As shown by Waterman and Volkoff (13) and discussed in the previous chapter, the $B^{11}$ resonance spectrum in Kernite simplifies considerably because of symmetry considerations if one orients $H_0$ in the $YZ$ plane of the crystal. Here $Y$ and $Z$ are two of the crystal symmetry axes (not to be confused with principal axes) and are mutually perpendicular.

In the case of Spodumene studied by Robinson the four $Al^{27}$ sites, which are all related by inversion have electric field gradients which not only have the same numerical values, but which are also oriented in an identical way with respect to the crystal axes. Thus from the point of view of the resonance spectrum of these nuclei, all the $Al^{27}$ sites in the unit cell, and therefore in the whole crystal, are completely equivalent to one another. This is the simplest possible kind of spectrum due to one kind of nucleus in a single crystal. Moreover, the existence of a two fold symmetry axis in addition to the two kinds of symmetry centres requires that the aluminum sites lie on these symmetry axes, and that one principal axis of the electric field gradient
tensor at the sites of the two nuclei coincides with the symmetry axis. On account of the above structure of Spodumene the direction of the external magnetic field can be so chosen as to give rise to a real Hamiltonian to be diagonalized to obtain energy levels. On the other hand, as we have already seen in Chapter II, the crystal structure of Kernite is such that it is convenient to choose the direction of the external magnetic field in the YZ plane which would not result in real Hamiltonians for the different B\textsuperscript{11} sites. Thus the present calculations are more general in so far as they deal with Hamiltonians with complex elements. As far as the eigen values are concerned there is no difference as both complex and real Hamiltonians give real values, but the eigen functions for a complex Hamiltonian are all complex. These considerations make the present calculations more complicated than in the previous case of Spodumene.

If $H_o$ is at an angle $\psi$ with the $Y$ axis and in the YZ plane, then the quantities in the above Hamiltonian matrix may be written as follows in units of $eQ \Phi zz$.

\[
\begin{align*}
A &= (-3/2) c \Gamma + 3 \\
B &= (-1/2) c \Gamma - 3 \\
C &= (1/2) c \Gamma - 3 \\
D &= (3/2) c \Gamma + 3
\end{align*}
\]

where

\[
\begin{align*}
a &= \kappa_1 \cos \psi + \nu_1 \sin \psi \\
b &= \kappa_2 \cos \psi + \nu_2 \sin \psi \\
c &= \kappa_3 \cos \psi + \nu_3 \sin \psi \\
\Gamma &= \sqrt{h_0/3/2} \frac{12}{eQ \Phi zz}
\end{align*}
\]
\( \lambda_1, \lambda_2 \) and \( \lambda_3 \) are defined as the direction cosines of the field gradient tensor principal axes \( x, y, z \) respectively with respect to the \( X \)-crystal axes, \( \lambda_1, \lambda_2 \) and \( \lambda_3 \) are direction cosines with respect to the \( Y \) crystal axis and \( \lambda_1, \lambda_2 \) and \( \lambda_3 \) are direction cosines with respect to the \( Z \) crystal axis.

The eigen values of the Hamiltonian, \( E \), are expressed in terms of the dimensionless quantity.

\[
\lambda = \frac{E}{\sqrt{\mathcal{E} \phi_{zz}}} \]

From the high field work of Waterman and Volkoff (13) the values of the direction cosines are given by the values in Table 1.

<table>
<thead>
<tr>
<th>Site</th>
<th>Axis</th>
<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>-0.76 ± 0.04</td>
<td>-0.60 ± 0.03</td>
<td>+0.21 ± 0.01</td>
</tr>
<tr>
<td>( E_{1,2} )</td>
<td>( Y )</td>
<td>+ (0.22 ± 0.03) + (0.05 ± 0.01) + (0.97 ± 0.02)</td>
<td>+ (0.60 ± 0.07) + (0.79 ± 0.07) + (0.01 ± 0.01)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( Z )</td>
<td>+ (0.37 ± 0.02) + (0.33 ± 0.02) + (0.865 ± 0.001)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

To make the calculations as accurate as possible the values of the direction cosines in Table 1 have been modified within the permissible range of error so that they would satisfy the orthogonality and normalization conditions.
In all of the following graphs showing energy levels and transition frequencies as a function of (Figures 2 to 15 inclusive), the units of energy and transition frequencies are \( \frac{eQ \Phi_{zz}}{12n} \) while the units of \( \Gamma \) are expressed in terms of the dimensionless quantity \( \Gamma = \frac{8 \mu H_0/eQ \Phi_{zz}}{1} \).

One unit of energy corresponds to almost 214 kc/sec while one unit in \( \Gamma \) corresponds to a field of about 156 gauss.
Figure 3.
Figure 4.

E-SITE

$\psi = 30^\circ$
Figure 6.

E-SITE

$\psi = 90^\circ$

Facing page 14
Figure 9.

Facing page 14
Figure 10.

F-SITE

ψ = 0°
Figure 13.
CHAPTER IV

NUMERICAL RESULTS FOR ENERGY LEVELS AND TRANSITION FREQUENCIES

Solution of the Hamiltonian

The computation of eigen values over a reasonable range of $\Gamma$ and for several angles is a tedious task. Fortunately, electronic computers have become almost commonplace aids to scientific research in the past few years, and the work of diagonalizing matrices can be performed in a much shorter time than by hand.

In March 1957, a computer ALWAC-III-E was installed by the University of British Columbia and has been used to carry out all the present calculations. Diagonalization of a matrix such as $\begin{bmatrix} 2 \end{bmatrix}$ and determination of eigen values and eigen functions takes about 3 hours using a desk computer while the machine does the same calculations within $3\frac{1}{2}$ minutes. It can be seen how useful these computers are to speed up the calculations. It would have been beyond the author's courage to undertake the calculations reported here without the aid of the computer.

Energy levels as a function of external magnetic field $H_0$ for $\varphi = 0^\circ, 30^\circ, 60^\circ, 90^\circ, 120^\circ$ and $150^\circ$ and transition frequencies as a function of field for $\varphi = 0$ and $\varphi = 90^\circ$ are shown in figures 2, 3, 4, 5, 6, 7, 8, and 9 for the E-sites. Energy levels and frequency transitions for $\varphi = 0^\circ$ and $\varphi = 90^\circ$
as a function of field in the case of F-sites are shown in figures 10, 11, 12 and 13. Calculations for $\gamma = 30^\circ, 60^\circ, 120^\circ$ and $150^\circ$ have been carried out but are not reported here.

The values for asymmetry parameters $\gamma$ and quadrupole coupling constants $\frac{eQ\phi_{zz}}{h}$ for both E and F sites are taken from the high field results of Waterman and Volkoff on Kernite (13). These are given in Table II below and are consistent with the pure quadrupole resonance frequencies ($H_0 = 0$) measured by Hearing (14).

<table>
<thead>
<tr>
<th>Site</th>
<th>Asymmetry parameter</th>
<th>Quadrupole coupling constant $eQ\phi_{zz}/h$</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>0.163 $\pm$ 0.101</td>
<td>2.563 $\pm$ 0.007 Mc/sec.</td>
</tr>
<tr>
<td>F</td>
<td>0.116 $\pm$ 0.010</td>
<td>2.567 $\pm$ 0.010 Mc/sec.</td>
</tr>
</tbody>
</table>

As might be expected the energy levels do not cross each other in any of the crystal orientations as in the case of Spodumene. In the case of crystals which have one of the principal axes coinciding with the crystal axis and the external magnetic field $H_0$ taken along this axis, the energy levels cross each other. Let us consider such an example. Let the nuclei under consideration have spin $3/2$ as in the case of $B^{11}$. Then in the Hamiltonian matrix $[2]$ the elements $h, h^\ast, i, i^\ast$ vanish and we are left with the following expression for the secular determinant.
We can break up the determinant into two 2 x 2 determinants by rearranging rows and columns so that the order instead of 1, 2, 3, 4 is 1, 3, 2, 4. The energy levels fall into two classes; class L states have mixtures of spin 3/2 and -1/2 and class M states have mixtures of spin 1/2 and -3/2. Due to the selection rule \( m = \pm 1 \) only transition between levels of different classes can occur and these energy levels can cross each other. To illustrate this, Figures 14 and 15 give the energy levels for \( H_0 \) along the z principal axis of one of the E and F sites respectively. It should be noted that these calculations would be difficult to verify experimentally as the remaining 3 sites (out of \( E_1, E_2, F_1, F_2 \)) would each give a complicated spectrum.

In the present case where no such orientation of the crystal as discussed above is possible for all \( B_11 \) sites, it is not possible to have class L and M states. The off diagonal elements of the Zeeman Hamiltonian lead to mixing of all spin states so that every eigen state of the Hamiltonian will be a mixture of all four possible spin states and the energy levels no longer cross one another. A total of 6 transitions will be possible in principle, since there will be a non-zero probability of transition between any two levels.
The system of numbering the energy states and transitions between them is shown in figure 2. The energy levels are numbered in order of decreasing energy and the transition between $i$ and $j$ levels is indicated by $\gamma_{ij}$. This convention is followed for all graphs of transition frequencies.

We can see from figure 11 where $\psi = 0$, the transition frequency for the F-site between levels 2 and 3 decreases gradually to about 900 K. c/s at $\Gamma = 2.5$ where it goes through a minimum and then we notice a gradual increase, while in figure 12 where $\psi = 90^\circ$ the transition frequency of $\gamma_{23}$ has a minimum of 250 K. c/s at $\Gamma = 3.2$. Similarly, many other transitions show characteristic minima or maxima whose frequency and position vary with orientation of the magnetic field. Most of these maxima and minima are in a frequency region relatively easy to attain experimentally and should be experimentally observable.
CHAPTER V

TRANSITION PROBABILITIES AND SIGNAL INTENSITIES

Theory

Nuclear resonance transitions are usually caused by a radio frequency magnetic field produced by r.f. current in a coil. The resonance condition is often detected by absorption of energy from the coil by the nuclear spins. In such a case, the signal intensity is proportional to the transition probability, aside from variations in signal intensity due to variations in other quantities such as line width, relaxation time, etc.

In an induction type spectrometer a signal voltage is produced by magnetic induction due to the r.f. nuclear magnetisation induced by the r.f. magnetic field which produces transitions. The signal voltage in an induction spectrometer will not necessarily be simply related to the transition probability as in the case of absorption spectrometer, except for the case of a nucleus which experiences only a magnetic interaction and therefore has $2I + 1$ equally spaced levels due to interaction with an external magnetic field.

For transitions between states which cannot be expressed as eigenstates of the operator $I_z$ for any coordinate system the signal intensity may not be the same for the two types of spectrometers. Recently a theory has been developed
which enables one to calculate how signal intensities for resonance between any pair of states may be related to the properties of these states for either absorption or induction spectrometers (15, 17). In order to apply this theory to Kernite, it must be generalized to the case of a complex Hamiltonian, as the theory was originally developed for real Hamiltonians in order to explain the signal intensities observed in Spodumene. Generalization of this theory to complex Hamiltonian is described below and is then applied to the calculation of signal intensities in Kernite.

Derivation of the Modified Bloch Equations

Consider the Hamiltonian of the nucleus of spin I, which interacts with arbitrary electric and magnetic fields. We split it into two parts, one $H_0$ which is time-independent and another $V$ which is time dependent and assume that eigen functions and eigen values of $H_0$ are known. Here $H_0$ is given by equations 1 and 2, while $V$ will be the Hamiltonian describing interaction between the nuclear magnetic moment and the r.f. magnetic field which produces transitions.

$$H_0 \psi_1 = E_1 \psi_1, \quad H_0 \psi_2 = E_2 \psi_2 \text{ etc.}$$

In general there will be $2I + 1$ energy levels, but we confine our attention to two of them, 1 and 2 which are assumed to be non-degenerate with respect to any other of the $2I + 1$ states.

The only important matrix elements of $V$ are assumed to be those of diagonal elements connecting states
Such would be the case to first order. In the present case $V$ is assumed to involve only magnetic interactions and we may write

$$V = \gamma \hbar \left[ I_u H_u + I_v H_v + I_w H_w \right] = \gamma \hbar \mathbf{I} \cdot \mathbf{H} \quad [5]$$

where $\gamma$ is the gyromagnetic ratio and $I_u$, $I_v$ and $I_w$ are components of the angular momentum operator $\mathbf{I}$ in an arbitrary coordinate system where axes are denoted by $u$, $v$, and $w$ respectively, while $H_u$, $H_v$ and $H_w$ are the components of the time magnetic field $\mathbf{H}$ in this coordinate system. The matrix elements between the states 1 and 2 are assumed to be known and we define

$$
\begin{align*}
(\psi_1^*/I_u/\psi_2) &= P \\
(\psi_1^*/I_v/\psi_2) &= iS \\
(\psi_1^*/I_w/\psi_2) &= T
\end{align*}
$$

$$
\begin{align*}
(\psi_2^*/I_u/\psi_1) &= P^* \\
(\psi_2^*/I_v/\psi_1) &= iS^* \\
(\psi_2^*/I_w/\psi_1) &= T^*
\end{align*}
$$

$P$, $S$ and $T$ can be easily found if the eigenfunctions $\psi_1$, $\psi_2$ are known.

The solution of the time dependent Schroedinger equation $i\hbar \dot{\psi} = (H_0 + V) \psi$ is assumed to be

$$\psi = a \psi_1 + b \psi_2$$

where the coefficients $a$ and $b$ are, in general, time dependent.

We now introduce three variables, the "time dependent" parts of the expectation values of $I_u$ and $I_v$ which are denoted
by \( I_u(t) \) and \( I_v(t) \) respectively and the population difference between the states 1 and 2, which is denoted by \( n \)

\[
\begin{align*}
I_u(t) &= (\psi^*/I_u/\psi)' = Pa^*b + P^*ab^* \quad [7] \\
I_v(t) &= (\psi^*/I_v/\psi)' = iSa^*b - iS^*ab^* \quad [8] \\
n &= a^*a - b^*b \quad [9]
\end{align*}
\]

The primes indicate that only the off diagonal matrix elements of \( I_u, I_v \) are considered in [7] and [8] respectively. As shown in Feynman et al (12) the time dependent Schrödinger equation can be expressed in terms of the quantities appearing in [7], [8] and [9] as follows

\[
\frac{d\vec{r}}{dt} = \vec{w} \times \vec{r} \quad [10]
\]

where

\[
\begin{align*}
r_1 &= ab^* + ba^* \quad [11] \\
r_2 &= -i (a^*b - ab^*) \quad [12] \\
r_3 &= a^*a - b^*b = n \quad [13]
\end{align*}
\]

It may be seen that \( r_1, r_2, r_3 \) are all real and \( \vec{w} \) is also a three vector defined by

\[
\begin{align*}
w_1 &= (V_{12} + V_{21}) / \hbar \quad [14] \\
w_2 &= i(V_{12} - V_{21}) / \hbar \quad [15] \\
w_3 &= w_0 = (E_1 - E_2) / \hbar \quad [16]
\end{align*}
\]

where \( V_{12} \) and \( V_{21} \) are the matrix elements between states 12 and 21 and they are given by
\[ V_{12} = \gamma \hat{n} (\psi_1^* / I_u H_u + I_v H_v + I_w H_w / \psi_2) \]
\[ = (P H_u + T H_w + i S H_v) \, \gamma \, \hat{n} \]  
\[ [17] \]
\[ V_{21} = \hat{n} (2^* / I_u H_u + I_v H_v + I_w H_w / 1) \]
\[ = (P^* H_u + T^* H_w - i S^* H_v) \, \gamma \, \hat{n} \]  
\[ [18] \]

\( w_1, w_2, w_3, r_1, r_2 \) and \( r_3 \) may therefore be written as

\[ w_1 = \gamma \left[ (P + P^*) H_u + (T + T^*) H_w + i(S - S^*) H_v \right] \]  
\[ [19] \]
\[ w_2 = \gamma \left[ i(P - P^*) H_u + (T - T^*) H_w - (S + S^*) H_v \right] \]  
\[ [20] \]
\[ w_3 = w_0 \]  
\[ [16] \]
\[ r_1 = \left( \frac{S + S^*}{m} \right) \bar{T}_u + i \left( \frac{P - P^*}{m} \right) \bar{T}_v \]  
\[ [21] \]
\[ r_2 = i \left( \frac{S - S^*}{m} \right) \bar{T}_u - \left( \frac{P + P^*}{m} \right) \bar{T}_v \]  
\[ [22] \]
\[ r_3 = n \]

where \( m = P^* S - P S^* \)

If \( P, S \) and \( T \) are real equations \([10]\) reduce to the phenomenological equations previously derived to explain the Spodumene results \((15, 17)\).

Furthermore, if the damping terms \(- \frac{1}{T_2}, - \frac{2}{T_2}, + \frac{n_0 - n}{T_1}\) are added to the three components of equation \([10]\) respectively, the following equations are obtained

\[ \frac{d r_1}{dt} = w_2 r_3 - w_3 r_2 - \frac{r_1}{T_2} \]  
\[ [24a] \]
\[ \frac{d r_2}{dt} = w_3 r_1 - w_1 r_3 - \frac{r_2}{T_2} \]  
\[ [24b] \]
\[ \frac{dn}{dt} = w_1 r_2 - w_2 r_1 + \frac{\mu_0 - n}{T_1} \] [24c]

These three equations are the analogs, for an arbitrary two level system of the phenomenological equations of Bloch and may be seen to reduce to them for \( I = 1/2 \), if the macroscopic magnetization of the spin system is identified with \( \mathbf{I} \), where \( \mathbf{I} \) is the expectation value of \( I \).

**Solutions of the Modified Bloch Equations**

We now solve the Modified Bloch Equation [17] with damping terms for the case of a linearly oscillating r-f field \( 2H_1 \cos wt \) where \( H_1 \) is oriented in the direction of the u axis.

\[
\begin{align*}
H_u & = 2H_1 \cos wt \quad [25a] \\
H_v & = 0 \quad [25b] \\
H_w & = 0 \quad [25c]
\end{align*}
\]

We will not go through the solution of the resulting equations in detail, but will outline the procedure, and give the results. We solve for the case of "slow passage" in the sense defined by Bloch; that is, we assume that any frequency or field modulation used has a sufficiently slow time variation that \( n \) attains a quasi-static value at any time and we can put \( \dot{n} = 0 \). Then taking \( n \) as constant, equations [24a] and 24b with damping terms may be converted to second order differential equations in \( r_1, r_2 \). The slow passage solutions are the particular solution of these equations. The values of \( r_1, r_2 \) which depend linearly on \( n \), are substituted into the third equation. The resultant equation for \( n \) contains some constant
terms plus terms proportional to \( \sin 2\omega t \) and \( \cos 2\omega t \). These time dependent terms are discarded. The procedure, if followed for the Bloch equations for magnetic resonance, corresponds to splitting the linear oscillating field into two components rotating in opposite senses and neglecting the component which rotates in the sense opposite to the nuclear magnetization vector. The neglected component only produces small nutations of the magnetization at the angular frequency \( 2\omega \). Here also, we could, in principle, split our linearly polarised field into effective and ineffective components, except that these components, instead of being simply circularly polarised, would be elliptically polarised. The criterion for choosing the effective component becomes a bit more tricky and, so, we adopt the above procedure. The final results are:

\[
\begin{align*}
  r_1 &= \frac{\mathcal{N}_0}{D} \frac{T_2}{2} (\Delta \omega T_2 K + L) \cos \omega t + (K - \Delta \omega T_2 L) \sin \omega t \quad [26] \\
  r_2 &= \frac{\mathcal{N}_0}{D} \frac{T_2}{2} (\Delta \omega T_2 L - K) \cos \omega t + (L + \Delta \omega T_2 K) \sin \omega t \quad [27]
\end{align*}
\]

where \( D \) is the saturation factor

\[
D = 1 + \frac{K^2 + L^2}{4} T_1 T_2 + (\Delta \omega)^2 T_2^2
\]

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

and

\[
K = 2 \gamma H_1 (P + P^*)
\]

\[
L = 2 \gamma H_1 i (P - P^*)
\]

In a crossed coil spectrometer, a pick-up coil is usually oriented perpendicular to \( H_1 \). An oscillatory voltage
of angular frequency $w$ is induced in the coil due to induced nuclear magnetization caused by the applied r-f field. Suppose the pick-up coil is assumed to be along the $v$ axis, then the induced nuclear magnetization along the axis of the coil is proportional to $I_v(t)$. It is therefore only necessary to calculate $I_v(t)$ in order to compare the induced voltage and hence the relative signal intensity for such a crossed-coil spectrometer. Using [8], [11], [12], [13], [26] and [27] we obtain,

$$I_v = \frac{N o T^2}{D} \left[ \begin{array}{c} \Delta w T_2 (SP^* - S^*P) + (SP^* + S^*P) \\ - \Delta w T_2 (SP^* + S^*P) + i(SP^* - S^*P) \end{array} \right] \begin{array}{c} \cos \omega t \\ \sin \omega t \end{array}$$

Unlike the case of the absorption spectrometer the signal voltage and hence the signal intensity is not proportional to the square of the matrix element ($PP^*$), except for the case of magnetic interactions alone, in which $P = S$.

To interpret equation [28], it should be noted that the terms involving $\Delta w T_2$ would give rise to a characteristic dispersion signal, while the terms not involving $\Delta w T_2$ would by themselves give an absorption type signal. It can be clearly seen, if $S$ and $P$ are real the term proportional to $\cos \omega t$ will have a pure absorption type signal (out of phase component) and term proportion to $\sin \omega t$ (in phase component) will just have a pure dispersion type signal. This is the case in ordinary nuclear magnetic resonance where no quadrupole interactions are present. The striking feature introduced by complex $P$ and $S$ is that both
in phase and out of phase components now should consist of a mixture of absorption and dispersion type signals and hence the line shape can in general be more complex than for pure absorption or pure dispersion. In fact an asymmetric line shape might be expected.

In the case in which \( H_1 \) is taken parallel to \( u \), it can be shown that \( I_u(t) \) is proportional to \( PP^* \) and this would give the same signal intensities as the absorption type spectrometer. Therefore a spectrometer which detects the nuclear resonance by induction but which only employs the same coil for detecting the nuclear resonance as is used for producing the r.f. field gives the same relative intensities as an absorption spectrometer.

The calculations for the signal intensities for absorption method have been carried out for 2 specific cases for E-sites. In the first case both \( H_1 \) and \( H_0 \) are taken parallel to crystal \( Y \) axis. In the second case \( H_1 \) is taken parallel to \( Z \) axis and \( H_0 \) is taken parallel to \( Y \) axis. The results of these calculations are given in Tables III and IV. From these results, it may be seen that some of the transitions would give very much weaker absorption signals than others. In general, as in the case of Spodumene (16), strong variation in the relative intensity of a line as the external magnetic field is varied, occurs in the regions near maxima or minima in the transition frequencies.

The values of \( P, S \) and \( T \) have been calculated for \( \psi = 0^\circ \) to \( \psi = 150^\circ \) in steps of \( 30^\circ \) as a function of the external magnetic field \( H_0 \) for both E and F sites and they
are available from Dr. M. Bloom, U.B.C. The calculation of signal intensities making use of these above values is quite straightforward for any orientation of the r-f field. As it is difficult to foresee all the experimental requirements, it may not be possible to get all the information from the present calculations, but one can calculate them without much difficulty on ALWAC-III-E computer at U.B.C. The programme written for the calculation of matrix elements and P, S and T are available from Dr. Bloom.

The results for signal intensities for induction type spectrometer have been given in Table V for \( \psi = 0 \) for the E-sites. In this calculation \( H_1 \) was assumed to be along the crystal Y axis and the pick-up coil along the crystal Z axis, e.g. in terms of the previous discussion, the crystal Y and Z axes are equivalent to the u and v axes respectively. Note that here it is necessary to calculate two quantities corresponding to the real and imaginary parts respectively of \( SP^\# \) (see equation 28) in order to completely describe the intensities.

It should be stated that these calculations are only presented here as sample calculations. Detailed calculations should be made to suit the experimental requirements. In particular, in regions where sharp variations are predicted, the calculations should be made using smaller intervals of \( \Gamma \) than chosen here in order to get a detailed prediction of the signal intensities.
TABLE III

Square of the matrix elements of the perturbing operator $V$ (in arbitrary units) for E-sites as a function of $\Gamma$ in the case where $H_1$ and $H_0$ are both parallel to $Y$ axis for all six possible transitions

<table>
<thead>
<tr>
<th>$\Gamma$</th>
<th>$\mathcal{V}_{12}$</th>
<th>$\mathcal{V}_{13}$</th>
<th>$\mathcal{V}_{14}$</th>
<th>$\mathcal{V}_{23}$</th>
<th>$\mathcal{V}_{24}$</th>
<th>$\mathcal{V}_{34}$</th>
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<td>.0416</td>
<td>.0675</td>
<td>.0053</td>
</tr>
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<td>.1373</td>
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<td>.0034</td>
</tr>
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</tr>
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</tr>
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</tr>
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TABLE IV

Square of the matrix elements of the perturbing operator $V$ (in arbitrary units) for E-sites as a function of $\Gamma$ in the case where $H_0$ is parallel to $Y$ axis and $H_1$ parallel to $Z$ axis for all six possible transitions

<table>
<thead>
<tr>
<th>$\Gamma$</th>
<th>$V_{12}$</th>
<th>$V_{13}$</th>
<th>$V_{14}$</th>
<th>$V_{23}$</th>
<th>$V_{24}$</th>
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TABLE V

Product of the matrix elements of the perturbing operation $V$ (in arbitrary units) for E-sites as a function of $\Gamma$ in the case where $H_0$ is parallel to $Y$ axis, pick-up coil parallel to $Z$ axis and r.f coil parallel to $Y$ axis for all six possible transitions. $\theta = 2i(S^R_P - S^R_P)$  $\gamma = 2(S^R_P + S^R_P)$

<table>
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<tr>
<th>$\Gamma$</th>
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<th>14</th>
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CHAPTER VI

CONCLUSIONS

From the theoretical study of induction and absorption spectra of $^{211}$ nuclei in a single crystal of Kernite, we can say that it would be interesting to do both types of experiments to investigate the theoretical results. An experimental check on the theoretical calculations presented here would represent the most detailed test yet on the general Hamiltonian describing quadrupole interactions in crystals. In the case of induction spectra, it would be interesting to study the shape of the line as the theoretical investigation show asymmetry in the line shape.
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