<table>
<thead>
<tr>
<th><strong>Title</strong></th>
<th>Solid State Chemical Exchange in Some Sodium Salts as Studied by 2D Nutation NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Author(s)</strong></td>
<td>Ohki, Hiroshi</td>
</tr>
<tr>
<td><strong>Citation</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Issue Date</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Text Version</strong></td>
<td>ETD</td>
</tr>
<tr>
<td><strong>URL</strong></td>
<td><a href="https://doi.org/10.11501/2964159">https://doi.org/10.11501/2964159</a></td>
</tr>
<tr>
<td><strong>DOI</strong></td>
<td>10.11501/2964159</td>
</tr>
</tbody>
</table>

Osaka University Knowledge Archive: OUKA

http://ir.library.osaka-u.ac.jp/dspace/

Osaka University
Solid State Chemical Exchange in Some Sodium Salts as Studied by 2D Nutation NMR

By
Hiroshi Ohkei
SOLID STATE CHEMICAL EXCHANGE IN SOME SODIUM SALTS

AS STUDIED BY 2D NUTATION NMR

BY

HIROSHI OHKI

DEPARTMENT OF CHEMISTRY

FACULTY OF SCIENCE

OSAKA UNIVERSITY

1990
Contents

Abstract 1

1. Introduction 3

2. Theory 6
   2.1 Liouville Representation in NMR 6
   2.2 2D nutation NMR 10
   2.3 Chemical Exchange Effect 22
   2.4 Chemical Exchange Effect on the 2D Nutation Spectrum 25

3. Simulation 31
   3.1 Principle 31
      3.1.1 Diagonalization of the Liouvillians 31
      3.1.2 Powder Averaging 37
      3.1.3 Line Broadening 40
      3.1.4 2D Fourier Transformation 40
   3.2 Simulation Procedure 41

4. Sample 45
   4.1 NaN0₂ and NaHgCl₃.2H₂O 45
   4.2 Na₂SeO₃ 45
   4.3 Naₓ₋₋ZrₓSiₓPₓ₋₋O₁₂ 45
5. Experiment

5.1 Sample Preparation

5.1.1 NaNO₂ and NaHgCl₃·2H₂O

5.1.2 Na₂SeO₃

5.1.3 NaₓZrₓSi₇P₃ₓO₁₂

5.2 2D Nutation NMR

6. Data Analysis

6.1 Nutation Spectrum

6.2 Data Analysis

7. Discussion

7.1 Summary of the Present Work

7.2 2D Nutation NMR

7.3 Chemical Exchange Effect

8. Appendix

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1.1</td>
<td>49</td>
</tr>
<tr>
<td>5.1.2</td>
<td>49</td>
</tr>
<tr>
<td>5.1.3</td>
<td>49</td>
</tr>
<tr>
<td>5.2</td>
<td>54</td>
</tr>
<tr>
<td>6.1</td>
<td>57</td>
</tr>
<tr>
<td>6.2</td>
<td>63</td>
</tr>
<tr>
<td>7.1</td>
<td>89</td>
</tr>
<tr>
<td>7.2</td>
<td>91</td>
</tr>
<tr>
<td>7.3</td>
<td>97</td>
</tr>
<tr>
<td>8.</td>
<td>A-1</td>
</tr>
</tbody>
</table>
Abstract

A new theoretical method which is based on the Liouville representation was established to describe the evolution of the quadrupolar spin system under the influence of strong rf field, which has been termed 'nutation'. The Liouville formalism was introduced to handle time development of the spin system and to construct the theoretical expression for the complex interactions between the rf field and the multilevel spin system. Although the dimension of the matrix to be determined becomes far larger than that based on standard density matrix or fictitious spin methods, the formalism with the Liouvillian can easily be coded for computation and therefore is much suitable for the calculation by big computers. Also the Liouville representation has a form which can incorporate effects other than spin interaction in a straightforward manner. This property makes it possible to apply the nutation method to chemically exchanging system.

The new method was coded by FORTRAN to prepare the general simulation program which is necessary for analyzing the experimental 2D nutation spectra. The program can be applied to quadrupolar nuclei with spin numbers 3/2 ~ 9/2 and to systems with and without chemical exchange.

The 2D nutation NMR experiments were conducted for $^{23}\text{Na}$ in several compounds. The $^{23}\text{Na}$ resonance in NaNO$_2$ and in NaHgCl$_3$.2H$_2$O was used to examine the optimal experimental conditions for the 2D nutation spectra and to evaluate the sensitivity of the spectra to the quadrupole coupling constant, $e^2Qq/h$, and the asymmetry parameter, $\eta$, of the electric field gradient at the site of the resonant nucleus.
The $^{23}$Na 2D nutation NMR was applied to Na$_2$SeO$_3$ to distinguish the three crystallographically nonequivalent Na sites in this compound. The quadrupole coupling constants at the individual sites could be determined and also $\eta$ was estimated for two of the three sites in this material.

Na$_{1+x}$Zr$_2$Si$_x$P$_{3-x}$O$_{12}$ has been known as a typical sodium ion conductor. The $^{23}$Na 2D nutation NMR was used to obtain the direct information on the sodium transport in this material. The spectrum was remarkably temperature dependent and indicated unambiguously that the sodium ions are exchanging between the two nonequivalent sites. The spectrum was analyzed by the new theoretical method developed here and the rate of the Na ion exchange was estimated at each temperature. It was found that the activation energy deduced from the nutation spectra differs significantly from that determined by a previous conductivity measurement. The large discrepancy between the two values was interpreted qualitatively by the following model. In the 2D nutation NMR, the spectra are governed by the local exchange of the Na ion between two sites, whereas the net ionic conduction must accompany the long-range ion transport through the formation of vacancy in addition to the fluctuational exchange.
1. Introduction

Solid state nuclear magnetic resonance (NMR) can provide the information on the local static structure of the solid phase and molecular or ionic motions in the solid. The line splitting in single crystal and the line shape in powdered or polycrystalline material can now be routinely analyzed to determine the local structure of solid. Very often the line shape varies with temperature reflecting the onset of some molecular or ionic motion in solid. The measurements of line characteristics as well as the relaxation behavior of the spin system as a function of temperature (or pressure in some cases) give fruitful information on the molecular motion excited in the solid.

In the (solid) powdered samples, the spectra are broadened by several interactions such as dipole-dipole interaction, chemical shifts, and so on. For the quadrupolar nuclei which have the spins \( I \) greater than \( 1/2 \), the structure of the spectrum is often determined by strong quadrupole interaction that is caused by the coupling between the nuclear electric quadrupole moment and the electric field gradient (EFG). The quadrupole interaction can be used to examine the local site symmetry of the resonant nucleus and the electronic structure of molecular and ionic species in the crystalline solid. The quadrupolar nuclei are also used as a powerful probe for the "slow" molecular motion in solid. In the case where the quadrupole interaction is sufficiently large, the usual pure nuclear quadrupole resonance can apply to determine the quadrupole coupling constant \( e^2 Q q / h \) and the asymmetry parameter of the electric field gradient \( \eta \). If the \( e^2 Q q / h \) is consider-
ably small, one observes the quadrupole interaction as a perturbation to the NMR. Sometimes the strength of the quadrupole interaction is comparable with those of other interactions. In such case the usual NMR on powdered specimen cannot separate the individual interactions.

Two- or multi-dimensional NMR methods evolve different interactions along different coordinate axes and examine the different interactions independently. 2D nutation NMR recently proposed is one of such methods. It separates the quadrupole interaction from chemical shift interaction and others by evolving these different interactions onto two directions. In this method one measures the central component of the spectrum which is perturbed by the second order quadrupole interaction for the half-integer spin system but, by evolving the spectrum onto different directions under a specific condition, one can pick up the quadrupole interaction in the form free from other interactions. An important character of the nutation NMR lies in that crystallographically nonequivalent sites can be distinguished and the quadrupole interaction parameters as well as the magnitude of the chemical shift at each site can be determined.

It seems promising to utilize the nutation NMR by making use of the most of its specific characters to examine the dynamic process, in other words, chemical exchange process between nonequivalent sites. Although the quadrupole interaction of deuterium has been widely used to trace the chemical exchange in solid state, there has not been developed any direct method to study the motion of the quadrupolar nuclei with half-integer spins in the solid state. Since in solid electrolytes and fast ionic conduc-
tors various ions play the main role and as many of these ions have half-integer spins, number of valuable information about the ionic motion can be obtained if the nutation NMR can be used to examine the motional process in solid.

In the present work, a theoretical formulation of the 2D nutation NMR method using a new technique based on the Liouville representation is given. Next a method to incorporate the chemical exchange into the theory of the nutation NMR will be developed. Then NaN02 and NaHgCl3·2H2O will be used to test the efficiency of this method for determination of the quadrupole interaction parameters. Na2SeO3 is chosen to demonstrate how to separate and distinguish any crystallographically nonequivalent sites in crystal. Finally a model ionic conductor, Na1+xZr2Si12P3-xO12, is chosen to examine the effect of the chemical exchange on 2D nutation NMR spectrum, and the data were analyzed by the simulation method. The applicability of the 2D nutation NMR for chemically exchanging system will be discussed.
2. Theory

2.1. Liouville Representation in NMR

General treatment of pulsed NMR spectroscopy has been done using time dependent density matrix formalism. Throughout the text in this thesis, however, the Liouville (superoperator) formalism [1] will be used to describe the time evolution of the spin system. Since the Liouville representation is not familiar to the most of chemists, it seems to be the due course to give brief introduction of this special formalism. The Liouville representation is suitable for handling complicated time development of the density matrix and is well adopted to computer implementation, because it has a transparent presentation of the commutator which is by all means needed in the calculation of the evolution of density matrix. Hereafter, several important properties of the Liouville formalism are summarized in comparison with the usual Schrödinger representation.

a) In the Schrödinger representation, the density matrix $\rho$ obeys the von Neumann equation of motion [2]

$$\frac{d\rho}{dt} = -i[H, \rho],$$  \hspace{1cm} (2.1.1)

where $H$ is the total Hamiltonian of the system in the frequency units. In the Liouville formalism, the elements of the density matrix form density superkets (basis sets) and the time dependence of the density superkets is determined by the Liouvillian $L$:

$$\frac{d\rho}{dt} = -iL\rho,$$  \hspace{1cm} (2.1.2)

where $\rho$ is the density superkets in the column form, i.e.,
\[ \rho = (\rho_1, \rho_2, \rho_3, \ldots, \rho_1, \rho_2, \ldots, \rho_{2n}) , \]

(2.1.3)

where \( n = 2l+1 \) and \( l \) is the spin. \( L \) is defined through the relation

\[ L = H \otimes E - E \otimes \dagger H , \]

(2.1.4)

where \( E \) is the unit operator which has the same dimension as \( H \), and \( \dagger H \) represents the transposed matrix of \( H \) and \( \otimes \) stands for the direct product \((3.1)\) of two matrices. (See appendix.)

When the Hamiltonian can be diagonalized by a Unitary matrix \( U \) through the similarity transformation :

\[ H^d = U^{-1} H U , \]

(2.1.5)

(\( H^d \) means diagonalized Hamiltonian,) then the Liouvillian can be diagonalized by the use of the same Unitary matrix :

\[ L^d = U^{-1} L U = (U^{-1} \otimes U^{-1})(H \otimes E - E \otimes \dagger H)(U \otimes U) = H^d \otimes E - E \otimes H^d , \]

(2.1.6)

It should be noted that while the Hamiltonian plays the role of the operator characterizing the time evolution as well as that of operator specifying the energy of the system, the Liouvillian plays the former role only. This can be seen by the fact that, according to (2.1.6), the eigenvalues of Liouvillian consist of the differences of eigenvalues of the corresponding Hamiltonian.

b) When the Hamiltonian can be separated into a large time-independent interaction \( H_0 \) and a much smaller term \( H_1 \), one often writes the equation of motion of the spin system
in the interaction representation which removes unnecessary
term $H_0$ from the Hamiltonian. In this case, the Liouvillian
can be written
\[ L = L_a + L_i , \]
where
\[ L_a = H_a \otimes \mathbb{E} - \mathbb{E} \otimes H_a , \]
\[ L_i = H_i \otimes \mathbb{E} - \mathbb{E} \otimes H_i . \]

Then the Liouville description of the interaction representation is expressed by
\[ \rho' = \exp (+i L_a t) \rho , \]
\[ L' = \exp (+i L_a t) L_1 \exp (-i L_a t) , \]
where $\rho'$ and $L'$ are density superkets and Liouvillian in the
interaction representation, respectively. Accordingly the
equation of motion of the density superkets becomes
\[ \frac{d\rho'}{dt} = -iL' \rho . \]

If the Liouvillian $L'$ is explicitly time-independent, Eq.
(2.1.11) can be solved formally:
\[ \rho'(t) = \exp (-iL' t) \rho(0) . \]

c) Another feature of the Liouville formalism is in its
convenience in calculating the observables. For example,
the magnetization along the $x$-axis is described in the
Schrödinger representation as
\[ M_x = \text{Tr}(1 x \rho) , \]
while in the Liouville formalism,
\[ M_{\alpha} = I_{\alpha} \rho , \]  

(2.1.14)

where \( I_{\alpha} \) is the operator in the row form.

Thus one can write physical quantities simply as a product of matrices and vectors.

---

**Appendix**

The properties of direct product are summarized as follows. Direct product of two matrices \( A \) and \( B \) of \( n \) dimensions is defined by

\[
A \times B = \begin{pmatrix}
a_{11}B & a_{12}B & \cdots & a_{1n}B \\
a_{21}B & a_{22}B & \cdots & a_{2n}B \\
\vdots & \vdots & \ddots & \vdots \\
a_{n1}B & a_{n2}B & \cdots & a_{nn}B
\end{pmatrix}
\]

Thus the resultant matrix has \( n^2 \) dimension. And

\[
(A + B) \otimes C = A \otimes C + B \otimes C ,
\]

\[
(A \otimes B)(C \otimes D) = AC \otimes BD ,
\]

where \( + \) has usual meaning of matrix sum.
2.2. 2D Nutation NMR

In the high magnetic field, the NMR spectra of quadrupolar nuclei that have the spins $I \geq 1$ consist generally of $2I+1$ lines due to quadrupole interaction. In the powdered or polycrystalline samples the angles between the external magnetic field and the principal axes of the electric field gradient (EFG) are distributed at random in each microcrystal and therefore the spectra show characteristic powder patterns as exemplified in Fig. 2.1. The powder patterns shown in Fig. 2.1 are ideal ones and if such spectral patterns are observed one can analyze the spectra to determine the quadrupole interaction parameters. In many cases, however, powder spectrum gives indistinct structure owing to strong quadrupole interaction and/or dipolar interaction; sometimes the former makes the spectrum spread over several hundred kHz and as a result causes the signal to be buried under the noise.

For half-integer spins, the central peak, that corresponds to the transition between the spin states $|+1/2\rangle \leftrightarrow |-1/2\rangle$, can be almost always observed because it is not affected by quadrupole interaction in the first order perturbation. Therefore it is meaningful to search for a method or methods to determine the quadrupole interaction parameters from observed central transition only. One method widely used is the line shape analysis of the normal one dimensional (1D) spectrum, which is governed by the second order quadrupole interaction. But one weak point of this method lies in the fact that the interactions other than the quadrupole interaction cause the line broadening and/or line shift and it becomes difficult to determine the
Figure 2.1
Simulated a) the first order and b) the second order powder lineshapes for $I = 3/2$ ($\eta = 0$).
parameters accurately. Especially when several crystallographically nonequivalent sites exist and the signals corresponding to the individual sites overlap with each other, it is very difficult to derive the quadrupole interaction parameters at each site from the 1D spectrum.

The two-dimensional (2D) nutation NMR is probably the most powerful tool in the situation when the direct analysis of the powder pattern cannot be applied. The 2D nutation NMR is applicable to the quadrupolar nuclei having half-integer spin [4]. The rate of the 'nutation', which represents the motion of the magnetization in the frame rotating at the frequency of the rf field, varies with the strength of the rf field relative to the quadrupole interaction. In that rotating frame, the strong rf field makes all original spin eigenstates \( |m_z \rangle \) mix and the degree of the mixing depends on the strength of the quadrupole interaction and rf field. Since the mixing of the spin states produces shift in the individual eigenstates, the measurements of the shift in the spin eigenvalues under irradiation of strong rf field can be used to obtain information about the quadrupole interaction. The experiment is based on a pulsed NMR in which one observes the free induction decays (FID's) by changing the rf pulse duration incrementally and one performs double Fourier transform to obtain the 2D nutation spectrum which provides quantitative information on the quadrupole interaction parameters.

The experiment can be divided into three time-domains (see Fig. 2.2). a) Preparation period: thermal equilibrium magnetization is established. b) Evolution period: the magnetization nutates around the rf field under the influ-
Figure 2.2
Schematic representation of 2D nutation NMR experiment.
ence of an interaction Hamiltonian, $H_1$, during $t_1$, and c) Detection period: the magnetization along x-y plane in the laboratory frame is detected under the influence of another interaction, $H_2$, in the duration $t_2$.

The Hamiltonians which work during the periods b) and c) consist of

$$H_1 = H_z + H_Q(n) + H_D + H_c \sigma + H_r r(t), \quad (2.2.1)$$
$$H_2 = H_z + H_Q(n) + H_D + H_c \sigma, \quad (2.2.2)$$

where $H_z$ is the Zeeman interaction, $H_q$ the quadrupole interaction, $H_D$ the dipole interaction, $H_c \sigma$ represents the chemical shift, and $H_r r$ is the coupling between the spin and the applied rf field. $\Omega$ represents the angle between the external static magnetic field and principal axes of EFG tensor. Their explicit forms are [2]

$$H_z = \omega_0 I_z = \gamma H_0 I_z, \quad (2.2.3)$$
$$H_Q(n) = \sum Q_e V_{-e}, \quad (2.2.4a)$$
$$Q_e = a[3I_z^2 - 1(I+1)/2, \quad (2.2.4a)$$
$$Q_{+1} = \sqrt{3}a[I_z I_x + I_z I_y]/4, \quad (2.2.4a)$$
$$Q_{+2} = \sqrt{3}a[I_z^2 /4, \quad (2.2.4a)$$
$$V_0 = V_{zz} /2, \quad (2.2.4a)$$
$$V_{+1} = (V_{xx} \pm iV_{xy}) / \sqrt{6}, \quad (2.2.4a)$$
$$V_{+2} = (V_{xx} - V_{yy} \pm 2iV_{xy}) /2/6, \quad (2.2.4a)$$
$$a = eQ/[(2I-1)], \quad (2.2.4b)$$
$$H_D = \sum I_i D I_j, \quad (2.2.5)$$
$$H_c \sigma = H_\sigma I, \quad (2.2.6)$$

-14-
and
\[ H_{r} = \omega_{1} \left[ i\chi \cos(\omega_{0} t) + i\chi \sin(\omega_{0} t) \right] , \]

where \( \omega_{0} \) is the nuclear Larmor frequency, \( \chi \) and \( \sigma \) are the dipole interaction and the chemical shift tensors, respectively, and \( \omega_{1} \) is the strength of the rf field in the frequency units. Note that the Liouvillians in the absence of the chemical shift does not produce any net shift of the spectrum. (Although the quadrupole interaction leads to an asymmetric powder pattern, the center of gravity of its spectrum does not change. Also, the dipolar interaction makes the spectrum split but the center of gravity of the spectrum does not move.)

Henceforth, we will always assume that the relative strength of the different interactions is \( H_{z} \gg H_{0} \approx H_{r} \gg H_{Q} , H_{c} \). This situation is realized in the case of nuclei with fairly large quadrupole interaction such as \( ^{23}Na , ^{39}K , \)
\( ^{59}Co , ^{93}Nb \) etc. The most important condition is that the pulse apparatus can provide very strong rf field. Under above conditions one can treat the quadrupole interaction as well as the chemical shift as a perturbation and can neglect weaker dipole interaction. Then quadrupole interaction can be expanded up to the second order terms as

\[ H_{0}' = H_{0}^{(1)} + H_{0}^{(2)} , \]

where
\[ H_{0}^{(1)} = e^{2} q Q / 8 I (2I-1) (3 \cos^{2} \theta - 1 + \eta \sin^{2} \theta \cos 2 \phi) \times \left[ 3 I_{z}^{2} - I(I+1) \right] = \omega_{0} \left[ I_{z}^{2} - I(I+1) / 3 \right] , \]

(2.2.9)
and

\[ H_{0}^{(2)} = \frac{-i(3e^2qQ/2l(2l-1))}{32\omega_0} \]

\[ \times (9(1-\cos^2\theta)^2-6\eta(1-\cos^4\theta)\cos2\phi \]

\[ +\eta^2(1+\cos^2\theta)^2\cos2\phi+4\eta^2\cos^2\theta(1-\cos^22\phi)) \]

\[ \times [2l_z^2-2l(l+1)+1] \]

\[ -9(1-\cos^2\theta)\cos^2\theta+6\eta(1-\cos^2\theta)\cos\theta\cos2\phi \]

\[ +\eta^2(1-\cos^2\theta)\cos^2\theta\cos^22\phi \]

\[ +\eta^2(1-\cos^2\theta)(1-\cos^22\phi)) \]

\[ \times 4[8l_z^2-4l(l+1)+1] \], \quad (2.2.10) \]

where, \( \theta \) and \( \phi \) are the polar and the azimuthal angles of the direction of the static magnetic field with respect to the principal axes of the EFG, respectively, and others have usual meanings. The chemical shift interaction is represented by

\[ H_{cs}^{\prime} = \sigma l_z \], \quad (2.2.11) \]

Usually one can assume that the second order quadrupole interaction is negligible in the presence of a strong rf pulse, and the chemical shift term can be included in the Zeeman term, the Hamiltonians in Eqs. (2.2.1-2) can be redefined to be

\[ H_1 = H_0^{(1)} + H_{rf} \], \quad (2.2.12) \]

and

\[ H_2 = H_0^{(1)} + H_0^{(2)} \]. \quad (2.2.13) \]

The density superkets (Eq. (2.1.10)) at a time \( t_1+t_2 \) becomes in the frame rotating at \( \omega_0 \) (interaction representa-
In Eq. (2.2.14) \( \rho(0) \) is the density superkets at thermal equilibrium. In the high temperature approximation, it yields

\[
\rho(0) = (1 - \frac{\hbar \omega_0 I_z}{kT}/(2I+1))
\]

assuming that the Zeeman coupling dominates other interactions. The unit ket \( 1 \) in Eq. (2.2.21) can be always disregarded in the calculation since it does not contribute to signal.

Hereafter, Eq. (2.2.14) is solved for \( I = 3/2 \) as an example with respect to each period, i.e., evolution and detection periods.

a) Evolution period

Before examining the general feature of the nutation
NMR, two limiting cases will be studied as an illustration.

In the evolution period an rf pulse, $H_1 = \omega_1 / \gamma$, is applied on the spin system. If the rf strength is much stronger than the quadrupole interaction, the spin system can be treated as if the quadrupole interaction is absent while the rf field is applied. Then the Hamiltonian becomes

$$H_1 = \begin{pmatrix} 0 & \sqrt{3} \omega_1 / 2 & 0 & 0 \\ \sqrt{3} \omega_1 / 2 & 0 & \omega_1 & 0 \\ 0 & \omega_1 & 0 & \sqrt{3} \omega_1 / 2 \\ 0 & 0 & \sqrt{3} \omega_1 / 2 & 0 \end{pmatrix}. \quad (2.2.22)$$

This Hamiltonian can be diagonalized through a similarity transformation by the orthogonal matrix:

$$R = \begin{pmatrix} \sqrt{3} & 1 & -1 & \sqrt{3} \\ -1 & \sqrt{3} & \sqrt{3} & 1 \\ -1 & \sqrt{3} & -\sqrt{3} & -1 \\ \sqrt{3} & 1 & 1 & -\sqrt{3} \end{pmatrix}. \quad (2.2.23)$$

and the corresponding eigenvalues are $-\omega_1 / 2$, $3\omega_1 / 2$, $\omega_1 / 2$, and $3\omega_1 / 2$. Then one can immediately show that the magnetization nutates around the rf field at the characteristic frequency $\omega_1$.

In the opposite case when the rf pulse strength is much smaller than the quadrupole interaction, the rf pulse can merely excites the central transition when the rf frequency satisfies nearly the resonance condition, and so no effective mixing of the eigenstates occurs. This is because the energy difference of the adjacent levels is quite different from each other. Hence one can pick up the components concerning with the central transition from the Hamiltonian.
and this has the eigenvalues $\pm \omega_1$. Therefore the motion of the magnetization is represented by the rotation at frequency of $2\omega_1$. In general, it can be shown that the magnetization corresponding to the central transition rotates at $(1+1/2)\omega_1$ \[^2\].

In summary, when quadrupole interaction is weak enough compared with the strength of the rf field, then the magnetization nutates at $\omega_1$, and in the opposite case the magnetization nutates at $(1+1/2)\omega_1$.

If the quadrupole interaction and the rf field are comparable in magnitude, the nutational motion becomes complex. The equation of motion of the spin system in such complex cases has been solved using several different techniques \[^5\]. In the present work a new technique based on the Liouville representation is introduced to solve the problem.

The matrix representation of the Hamiltonian in the period $t_1$ can be written as

\[
H' = \begin{pmatrix} 0 & \omega_1 \\ \omega_1 & 0 \end{pmatrix},
\]

and this has the eigenvalues $\pm \omega_1$. Therefore the motion of the magnetization is represented by the rotation at frequency of $2\omega_1$. In general, it can be shown that the magnetization corresponding to the central transition rotates at $(1+1/2)\omega_1$ \[^2\].

In summary, when quadrupole interaction is weak enough compared with the strength of the rf field, then the magnetization nutates at $\omega_1$, and in the opposite case the magnetization nutates at $(1+1/2)\omega_1$.

If the quadrupole interaction and the rf field are comparable in magnitude, the nutational motion becomes complex. The equation of motion of the spin system in such complex cases has been solved using several different techniques \[^5\]. In the present work a new technique based on the Liouville representation is introduced to solve the problem.

The matrix representation of the Hamiltonian in the period $t_1$ can be written as

\[
H_1 = \begin{pmatrix} \omega_0 & \sqrt{3}\omega_1/2 & 0 & 0 \\ \sqrt{3}\omega_1/2 & -\omega_0 & \omega_1 & 0 \\ 0 & \omega_1 & -\omega_0 & \sqrt{3}\omega_1/2 \\ 0 & 0 & \sqrt{3}\omega_1/2 & \omega_0 \end{pmatrix},
\]

where $\omega_0$ is defined in Eq. (2.2.9). This Hamiltonian can be diagonalized through the similarity transformation by the orthogonal matrix \[^6\].

-19-
\[
Q = \begin{pmatrix}
\cos \theta & -\sin \theta & -\sin \theta & \cos \theta \\
\sin \theta & \cos \theta & \cos \theta & \sin \theta \\
\sin \theta & -\cos \theta & -\cos \theta & -\sin \theta \\
\cos \theta & \sin \theta & -\sin \theta & -\cos \theta
\end{pmatrix} / \sqrt{2}.
\]

(2.2.26a)

\[
\tan 2\theta_1 = (\sqrt{3}/2) \omega_1 / (\omega_0 + \omega_1/2),
\]

(2.2.26b)

and the corresponding eigenvalues are

\[
\lambda_1 = \omega_1/2 + (\omega_1^2 + \omega_0^2 - \omega_1 \omega_0)^{1/2},
\]

\[
\lambda_2 = \omega_1/2 - (\omega_1^2 + \omega_0^2 - \omega_1 \omega_0)^{1/2},
\]

\[
\lambda_3 = -\omega_1/2 - (\omega_1^2 + \omega_0^2 + \omega_1 \omega_0)^{1/2},
\]

\[
\lambda_4 = -\omega_1/2 + (\omega_1^2 + \omega_0^2 + \omega_1 \omega_0)^{1/2}.
\]

(2.2.27)

The Liouvillian can be diagonalized by taking account of Eq. (2.1.6) and it leads to the density superkets at the end of the pulse as

\[
\rho' (t_1) = R \exp (-i L^{d} t_1) R^{-1} \rho (0),
\]

(2.2.28a)

or

\[
\rho'_{j} (t_1) = \sum [R_{j} k R_{k} \rho (0)] \exp (-i \lambda_{l} t_1),
\]

(2.2.28b)

where \(\lambda_{l}\) is the l-th eigenvalue of the Liouvillian. In the above Eq. (2.2.28b), \(A_{j} = \sum [R_{j} k R_{k} \rho (0)]\) is called the 'transition amplitude' which represents the intensity of the component with the frequency \(\lambda_{l}\).

b) Detection period

After the rf pulse field is switched off, the Hamiltonian (also the Liouvillian) is diagonal and the density superkets at a time \(t_1 + t_2\) is given by

\[
\rho' (t_1 + t_2) = \exp (-i L^{2} t_2) \rho' (t_1).
\]

(2.2.29)
A lengthy manipulation yields the result that the signal corresponding to the central transition at a given orientation of the principal axes of the EFG with respect to $H_0$ is proportional to

$$S(t_1+t_2) = \left[3\sin\theta \sin\phi - (1-\cos\theta)(1+\cos\phi)\right] \sin(\lambda_3 - \lambda_1) t_1 \sin(\lambda_4 - \lambda_1) t_1 \sin(\lambda_3 - \lambda_2) t_1 \sin(\lambda_4 - \lambda_2) t_1 \exp(-i\omega_0^{(2)} t_2),$$  

(2.2.30)

where $\omega_0^{(2)}$ is the second order quadrupole shift of the central transition expressed by [7]

$$\omega_0^{(2)} = \frac{(e^2 q Q/h)^2}{192\omega_0} \times \left[9(1-\cos^2\theta)^2 - 6\eta(1-\cos^2\theta)\cos^2\phi \right. \left. + \eta^2(1+\cos^2\theta)(1-\cos^2\phi) \right] \cos^2\theta \cos^2\phi \left. -72(1-\cos^2\theta)(1-\cos^2\phi) \right] .$$  

(2.2.31)

Eq. (2.2.30) indicates that four of six transitions between the four eigenvalues contribute to the spectrum and their transition frequencies can be determined by numerical analysis of the spectrum. It should be noted that Eq. (2.2.30) consists of two parts: one is the nutation which is merely a superposition of sine functions of $t_1$, and the other depends on $t_2$ and is governed by the second order quadrupole interaction.
2.3. Chemical Exchange Effect

Chemical exchange means that the nucleus jumps between the 'sites' whose environments are different from each other, i.e., crystallographically nonequivalent sites in solids.

The basic assumption of the chemical exchange is that the principle of detailed balance between the sites is satisfied, i.e.,

$$p_j k_{ji} = p_i k_{ij}, \quad (2.3.1)$$

where $p_i$ stands for the thermal equilibrium population of the $j$-th site and $k_{ji}$ represents the exchange rate from the $j$-th to $i$-th site. Then one can write the exchange matrix for $m$ sites:

$$K = \begin{pmatrix}
  k_{11} & k_{12} & \ldots & k_{1m} \\
  k_{21} & k_{22} & \ldots & k_{2m} \\
  \vdots & \vdots & \ddots & \vdots \\
  k_{m1} & k_{m2} & \ldots & k_{mm}
\end{pmatrix}, \quad (2.3.2)$$

where the diagonal component $k_{ii}$ is the rate of jump from $i$-th site to another, i.e., the reciprocal of the average life time at the $i$-th site. The sign of $k_{ii}$ is taken to be negative (or zero). Each column must satisfy the following relation

$$k_{1j} + k_{2j} + \ldots + k_{mj} = 0. \quad (2.3.3)$$

Another assumption adopted here is that the spin-spin interaction between the sites is extremely small and can be neglected. This assumption makes possible to describe the Liouvillian and the density superkets in a simple form.
In principle, in the case where the chemical exchange occurs among the m sites, the density superkets $\rho$ is defined by [8]

$$\rho = \rho^{(1)} \otimes \rho^{(2)} \otimes \ldots \otimes \rho^{(m)} , \quad (2.3.4)$$

where $\rho^{(j)}$ represents the density superkets at the j-th site and $\otimes$ means the direct product of the kets. Eq. (2.3.4) tells that the cross terms between the density superkets at different sites should be calculated in order to describe the time evolution of the system. Since such cross terms appear mainly as a result of the interaction between spins at different sites, and fortunately, the spin-spin interaction between quadrupolar nuclei is usually very weak, one can ignore this type of interaction. Then, the total density superkets can be reduced as follows:

$$\rho = \rho^{(1)} \oplus \rho^{(2)} \oplus \ldots \oplus \rho^{(m)} , \quad (2.3.5)$$

where $\oplus$ means the direct sum of the density superkets. Similarly, the Liouvillian consists in principle of complex components if we take account of the interaction between the different sites. However, if we disregard the spin-spin interaction as mentioned above, the Liouvillian can be written in a simple form as

$$L = \begin{bmatrix}
L^{(1)} & 0 & 0 & \ldots & 0 \\
0 & L^{(2)} & 0 & \ldots & 0 \\
0 & 0 & L^{(3)} & \ldots & 0 \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
0 & 0 & 0 & \ldots & L^{(m)}
\end{bmatrix} , \quad (2.3.6)$$

where $L^{(j)}$ is the Liouvillian corresponding to the j-th
When the chemical exchange occurs, under the assumption that the exchange between the sites is instantaneous, the spin does not change its state during the jump. In other words no relaxation occurs in the course of the exchange process. Then

\[
\frac{dp}{dt} = -(iL+K)p,
\]  

(2.3.7)

and

\[
K = \begin{bmatrix} k_{11} & k_{12} & k_{13} & \ldots & k_{1n} \\ k_{21} & k_{22} & k_{23} & \ldots & k_{2n} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ k_{n1} & k_{n2} & k_{n3} & \ldots & k_{nn} \end{bmatrix} \otimes \text{Ex},
\]  

(2.3.8)

where Ex is \((2l+1)^2\) dimensional unit matrix.
2.4. Chemical Exchange Effect on the Nutation Spectrum

In this section, two-site exchange is examined for simplicity but the extension to the general multisite case is straightforward.

In usual treatment of the chemical exchange, the effect of chemical exchange on the spin system is neglected during the short rf pulse so as to simplify the problem. But in this work, the exchange of spins should be taken into account because it has severe effect on the nutation spectrum.

The Liouvillians corresponding to the j-th site are

\[ L^{(j)}_1 = L^{(j)}_Q + L^{(j)}_{CS} \]
\[ L^{(j)}_2 = L^{(j)}_Q + L^{(j)}_{CS} + L_{rf} \]

where \( L^{(j)}_Q \) and \( L^{(j)}_{CS} \) stand for quadrupole interaction and chemical shift at the j-th site, respectively. The exchange matrix becomes

\[
K = \begin{pmatrix}
  k_1 & -k_1 \\
  -k_2 & k_2
\end{pmatrix} \otimes E_k .
\]

Thus the density superkets at a time \( t_1 + t_2 \) becomes

\[
\rho(t_1 + t_2) = \exp\left(-i(L_{2} + K)t_2\right) \exp\left(-i(L_{1} + K)t_1\right) \rho(0) ,
\]

where \( L_{1} \) and \( L_{2} \) are the Liouvillians in the presence and absence of the rf pulse, respectively.

Now two limiting cases are examined.

1) Slow motion regime : \( k_1, k_2 \ll H_0, H_{rf} \)

In this case the chemical exchange effect can be treated as a perturbation because the effect on the spectrum from
the chemical exchange is small compared with that from the quadrupole and rf couplings. Then one can diagonalize the Liouvillian alone by means of the orthogonal matrix Eq. (2.2.26):

\[ L^d = \begin{pmatrix} L^{(1)} & 0 \\ 0 & L^{(2)} \end{pmatrix} \begin{pmatrix} Q^{(1)(1)} & 0 \\ 0 & Q^{(1)(2)} \end{pmatrix} \begin{pmatrix} 0 & Q^{(1)} \\ L^{(1)} & 0 \end{pmatrix} \begin{pmatrix} 0 & Q^{(2)} \\ 0 & L^{(2)} \end{pmatrix} = \begin{pmatrix} L^d^{(1)} & 0 \\ 0 & L^d^{(2)} \end{pmatrix}. \]  

(2.4.4)

And the exchange matrix becomes

\[ K^e = \begin{pmatrix} k_1 E_k & -Q^{(1)(1)} k_2 Q^{(2)} \\ -Q^{(2)(1)} k_1 Q^{(1)} & k_2 E_k \end{pmatrix}. \]  

(2.4.5)

According to the perturbation theory, the diagonal terms of the exchange matrix should cause the change of the spectrum in the first order. Hence the line width of the peak corresponding to each site is determined by the exchange rate \( k_1 \) and \( k_2 \), respectively.

ii) Fast Motion Regime : \( k_1, k_2 \gg H_0, H_{rf} \)

In the opposite case, one must diagonalize the exchange matrix and treat the quadrupole and rf pulse as the perturbation. To diagonalize the exchange matrix, one must symmetrize the exchange matrix if it is not symmetric. This symmetrization can be done by the matrix \( P \),

\[ P_{ij} = \sqrt{p_i} \delta_{ij}. \]  

(2.4.6)

through the similarity transformation, where \( \delta_{ij} \) stands for the Kronecker's delta. The Liouvillian is not altered and the exchange matrix becomes
This can be diagonalized by

\[ K' = \begin{bmatrix} \cos \phi & -\sin \phi \\ \sin \phi & \cos \phi \end{bmatrix} \begin{bmatrix} -k_1 & k' \\ k' & -k_2 \end{bmatrix} \begin{bmatrix} \cos \phi & \sin \phi \\ -\sin \phi & \cos \phi \end{bmatrix} \otimes E_x , \]

\[ = \begin{bmatrix} -(k_1 + k_2) & 0 \\ 0 & 0 \end{bmatrix} \otimes E_x , \]

(2.4.8a)

\[ \tan 2\phi = 2k'/(k_1 - k_2) , \]

(2.4.8b)

and so the Liouvillian is expressed as

\[ L' = \begin{bmatrix} L^{(1)} + L^{(2)} & 0 \\ 0 & L^{(1)} + L^{(2)} \end{bmatrix} + (L^{(1)} - L^{(2)}) \begin{bmatrix} \cos 2\phi & \sin 2\phi \\ \sin 2\phi & -\cos 2\phi \end{bmatrix} . \]

(2.4.9)

Here the diagonal blocks of the Liouvillian determine predominantly the spectral appearance. However the components of the Liouvillian corresponding to \(-k_1 + k_2\) decrease so fast that these can be neglected. Then the spectrum is characterized by :

\[ (1-\cos 2\phi)L^{(1)} + (1+\cos 2\phi)L^{(2)} = p_1 L^{(1)} + p_2 L^{(2)} . \]

(2.4.10)

Thus the spectrum is described by the use of the weight-averaged Liouvillian. In the case of the two-site jump the time-averaged spectrum shows a characteristic pattern de-
pending on the relative orientation of the principal axes of the EFG tensor at the two sites. Hence the analysis of the spectrum at fast motion regime can determine the angle between the EFG principal axes at the two sites.

iii) Intermediate cases

The spectrum will change its appearance drastically if the rate of chemical exchange becomes comparable to the difference of the nutation frequencies at different sites. Therefore the 2D nutation spectrum can be applied to chemically exchanging systems to determine the rate of exchange when it is of the comparable order with $e^2 Q q / h$ (and also with $\omega_1$). For the analysis of the complicated spectrum in the above region one must simulate the nutation spectrum with the exchange rate as a variable parameter.
References

[1] See, for example.
R.R. Ernst, G. Bodenhausen, and A. Wokaun,

J. Jeener,
_Superoperators in Magnetic Resonance_,

[2] A. Abragam,
_Principle of Magnetic Resonance_,

[3] G. Arfken,
_Mathematical Methods for Physicists_,

[4] A. Samoson and E. Lippmaa,
A. Samoson and E. Lippmaa,

R. Janssen, and W.S. Veeman,
P.P. Man,
[6] L. Pandey, S. Towta, and D.G. Hughes, 

[7] D.R. Torgeson and R.G. Barnes, 

[8] J. Sandström, 
Dynamic NMR Spectroscopy, Academic Press, 1982

[9] T.E. Bull, 
3. Simulation

3.1. Principle

3.1.1. Diagonalization of the Liouvillians

In the case when only one kind of site exists, the calculation is straightforward since the analytical expression given in Sec. 2.2 can be applied. Even when several nonequivalent sites exist in the crystal and when no chemical exchange occurs, the whole spectrum can be represented by the superposition of the spectrum corresponding to each site. In the case where the chemical exchange occurs, one should calculate the Eq. (2.4.3), or equivalent to say, one must diagonalize the matrices in each period numerically. Because the matrices \( L_1 + K \) and \( L_2 + K \) in Eq. (2.4.3) are complex and non-Hermitian and have very large dimension of \((2I+1)^2 \times \) (number of site), they cannot be diagonalized directly by the usual methods. Then several modifications on the matrices must be made.

At first, the exchange matrix should be transformed by the matrix \( P \) so as to symmetrize the whole matrix. Then,

\[
L^1_{\text{S1}} \equiv (P^{-1} \otimes E_0)(L_1 + K)(P \otimes E_0) = L_1 + K^S , \quad (3.1.1a)
\]
\[
L^2_{\text{S2}} \equiv (P^{-1} \otimes E_0)(L_2 + K)(P \otimes E_0) = L_2 + K^S , \quad (3.1.1b)
\]

where

\[
K^S = (P^{-1} \otimes E_0)K(P \otimes E_0) , \quad (3.1.1c)
\]

and \( P \) is defined by Eq. (2.4.6). Then it is proved that the matrix \( L^S_{\text{S1}} \) (and also \( L^S_{\text{S2}} \)) can be diagonalized by a complex orthogonal matrix. (The complex orthogonal matrix means
that the multiplication of its transposed matrix and itself yields the unit matrix.) It should be noted that the exchange matrix is symmetrized by the above transformation which is however independent of the Liouvillian at each site.

In the evolution period when rf pulse is applied, another transformation is needed to reduce the dimension of the matrix to be diagonalized. This can be achieved by transforming the $l_z$ basis' to $l_x$ basis [11]. When the rows and the columns are suitably interchanged, the Liouvillian at the $j$-th site $L_j$ can be factorized so as to have a block-diagonal structure whose blocks have the dimension $(2l+1)^2/4 = 4$.

$$L_j' = (RT)^{-1} L_j (RT)$$

$$= \begin{pmatrix} A_j & 0 \\ B_j & B_j^t \\ 0 & A_j^t \end{pmatrix},$$

and density superket at the site $j$ becomes

$$\rho_j' = (RT)^{-1} \rho_j,$$

where $R = R \otimes R$ ($R$ is defined in Eq. (2.2.23)) is an

* 'l_z basis' means that the axis parallel to the static external magnetic field is the quantization axis. Thus $l_z$ becomes good quantum number. Also, 'l_x basis' means that the axis parallel to the rf field is the quantization axis and in this choice of the basis, $l_x$ is good quantum number.
orthogonal matrix which operates to transform the basis from $l_z$ to $l_x$, and $T$ the matrix to interchange the rows and the columns. By this transformation, the exchange matrix remains unchanged. The explicit matrix forms of the block matrices $A$, $A'$, $B$, and $B'$ for $I = 3/2$ are:

\[
A_j = \begin{bmatrix}
0 & \sqrt{3}\omega_j & -\sqrt{3}\omega_j & 0 \\
\sqrt{3}\omega_j & -2\omega_j + 4\omega_1 & 0 & -\sqrt{3}\omega_j \\
-\sqrt{3}\omega_j & 0 & 2\omega_j - 4\omega_1 & \sqrt{3}\omega_j \\
0 & -\sqrt{3}\omega_j & \sqrt{3}\omega_j & 0
\end{bmatrix} / 2 ,
\]  
(3.1.4a)

\[
B_j = \begin{bmatrix}
2\omega_j + 2\omega_1 & \sqrt{3}\omega_j & \sqrt{3}\omega_j & 0 \\
\sqrt{3}\omega_j & 6\omega_1 & 0 & \sqrt{3}\omega_j \\
\sqrt{3}\omega_j & 0 & -2\omega_1 & \sqrt{3}\omega_j \\
0 & \sqrt{3}\omega_j & \sqrt{3}\omega_j & -2\omega_j + 2\omega_1
\end{bmatrix} / 2 ,
\]  
(3.1.4b)

\[
B'_j = \begin{bmatrix}
-2\omega_j & -2\omega_1 & -\sqrt{3}\omega_j & -\sqrt{3}\omega_j & 0 \\
-\sqrt{3}\omega_j & -6\omega_1 & 0 & -\sqrt{3}\omega_j \\
\sqrt{3}\omega_j & 0 & -2\omega_1 & -\sqrt{3}\omega_j \\
0 & \sqrt{3}\omega_j & \sqrt{3}\omega_j & 2\omega_j - 2\omega_1
\end{bmatrix} / 2 ,
\]  
(3.1.4c)

\[
A'_j = \begin{bmatrix}
0 & \sqrt{3}\omega_j & \sqrt{3}\omega_j & 0 \\
\sqrt{3}\omega_j & 2\omega_j + 4\omega_1 & 0 & \sqrt{3}\omega_j \\
\sqrt{3}\omega_j & 0 & -2\omega_j - 4\omega_1 & -\sqrt{3}\omega_j \\
0 & \sqrt{3}\omega_j & -\sqrt{3}\omega_j & 0
\end{bmatrix} / 2 ,
\]  
(3.1.4d)

where $\omega_j$ represents the first order quadrupole interaction at the site $j$. The corresponding density superkets at $j$-th
site transformed as the Liouvillian are given by:

$$\rho^i_j = \frac{1}{\sqrt{3}} \left( \begin{array}{cccc}
0 & 0 & 0 & 0 \\
0 & 3 & 0 & -\sqrt{3} \\
0 & 0 & 3 & -\sqrt{3} \\
0 & 0 & 0 & 0 
\end{array} \right).$$  \hfill (3.1.5)

Because the elements of the density superkets corresponding to the matrices A and A' on the basis Ix are zero at thermal equilibrium, these can be disregarded. Because the matrices B and B' are complex conjugates with each other and the density superkets corresponding to B and B' are identical at time zero, the matrix to be diagonalized is reduced to

$$L^i_j = \sqrt{3} \left( \begin{array}{cc}
B_1 & k \varepsilon \varepsilon \\
k \varepsilon \varepsilon & B_2 - k \varepsilon \varepsilon 
\end{array} \right),$$  \hfill (3.1.6)

where $B_j$ is given in Eq. (3.1.4b) and $\varepsilon \varepsilon$ is the unit matrix which has the same dimension as $B_j$'s.

Although the Ix basis is very convenient for diagonalizing the Liouvillian, it is not suitable for calculation of the FID's since the transition observed in the detection period is labelled by the transition between the quantum number $m_z$, which is the eigenvalues of Iz. Then it has to be put back to the Iz basis.

In the detection period, the Liouvillian is diagonal and exchange matrix merely couples the density superkets with the same labels belonging to different sites. Then one calculates a matrix which consists of the elements concerning only with the central transition. Because the dimension of its matrix, $L^i_j$, is the number of the sites, this matrix can be easily diagonalized compared with that in the evolution period.

Then the FID signal at a time $t_1+t_2$ becomes
\( S(t_2, t_1) = I_x \rho(t_2, t_1) \)
\( = \sum P_{i,j} Q_{i,j} \exp[-i L_{d_j} t_2] Q_{2^{-1},j} \)
\( \times R_{i,1} Q_{1,1} \exp[-i L_{d_i} t_1] Q_{1^{-1},1} \rho_x(0) \).

(3.1.7)

where \( Q_1 \) and \( Q_2 \) are complex orthogonal matrices which diagonalize \( L_{d_1} \) and \( L_{d_2} \), respectively.

The Liouvillians \( L_{d_1} \) and \( L_{d_2} \) have special properties:

It is symmetric (or can be symmetrized by the method described in Sec. 3.1), and all their elements distant from the diagonal element by a certain fixed number, which denotes a band width, are zero. These properties can be fully utilized to perform the numerical diagonalization.

There are many possible methods to do this but the present work adopts a method which consists of two stages [2].

First is to find a transformation which reduces the band width and gives the symmetric tridiagonal matrix but keeps the symmetric and bandform characters of the Liouvillians unchanged. This is accomplished by the successive Jacobi rotation in the plane of \( i \) and \( j = i + 1 \) which is the orthogonal transformation.
This procedure is for eliminating the matrix element at \((i, i+1)\). Although the Jacobi rotation creates a new non-zero element at \((i+b, j+b)\), where \(b\) is the band width of the matrix, a series of rotations gives rise to result that \(i+b\) or \(j+b\) is greater than the dimension of the matrix. Thus one can eliminate the element without creating another one. These transformations are continued until the matrix is tridiagonalized. Then the Liouvillian becomes

\[
L' = \Pi(J^{-1})L\Pi J,
\]

where \(L'\) has zero off-diagonal elements except those immediately adjacent to the diagonal one.

Secondly, the matrix is diagonalized by the QR method. Let \(A_0\) be a general symmetric \(n\)-dimensional matrix to be diagonalized. An origin-shift parameter \(S_i\) is suitably selected so as to realize the factorization \(A_i - S_i E = Q_i R_i\), where \(Q_i\) is a complex orthogonal matrix and \(R_i\) is an upper triangular matrix, then \(A_{i+1} = Q_i^{-1} A_i Q_i\) can be obtained. When this procedure is iterated it can be shown that this series of matrices similar to \(A_0\) generally tends to an upper...
triangular matrix. Since \( A_\omega \) is a tridiagonal matrix, the resultant matrix is diagonal and its diagonal elements give the eigenvalues in this case.

In each step of iteration, the origin shift is chosen to be one of the two eigenvalues of \( 2\times 2 \) submatrix at the bottom right-hand corner that has smaller modulus. The Jacobi rotations to effect the decomposition \( A_j - s_j E = Q_j R_j \) is used to triangularize \( A_j \), i.e., in the rotations in the planes \((i,r+1)\) where \( i=1,2,\ldots,r \), rotation angle is determined such that the element \((r+1,1)\) becomes zero.

The actual diagonalization subprogram is the modification of the one in the NUMPAC routine in the Nagoya University. First stage of the tridiagonalization is referred to [2]. And second stage is QR method modified by the use of complex orthogonal matrix instead of Unitary matrix.

3.1.2 Powder Averaging

In the powdered samples, the crystals are oriented at random with respect to the magnetic field. Thus one must designate the orientation of the principal axes of the EFG tensor with respect to the static magnetic field so as to perform the powder averaging [3]:

\[
f(t_2,t_1) = \int d\phi \int \sin \theta d\theta \, S(t_2,t_1) . \tag{3.1.10}
\]

The coordinate transformation from the laboratory frame to the crystalline frame (a coordinate fixed in the crystalline specimen) is represented by the rotation:
where \( \theta \) and \( \phi \) are the polar and the azimuthal angles of the crystalline frame referred to the direction of the static magnetic field, respectively. When the EFG principal axes at the site \( j \) are indicated by the Euler angles \( \alpha, \beta, \) and \( \gamma \) in the crystalline frame by:

\[
R_j = \begin{pmatrix}
\cos \alpha \cos \beta & \sin \alpha & 0 \\
-\sin \alpha \cos \beta & \cos \alpha & 0 \\
-\sin \beta & 0 & 1
\end{pmatrix},
\]

then the matrix representing the rotation from the orientation of the magnetic field to the EFG principal axes is given by

\[
R_j' = R_j R_c.
\]

Here, the terms needed in the actual calculation are

\[
\begin{align*}
Z_j^2 &= \cos^2 \theta_j, \\
X_j^2 - Y_j^2 &= \sin^2 \theta_j \cos 2 \phi_j,
\end{align*}
\]

where

\[
\begin{align*}
x_j &= [\cos \alpha \cos \beta \cos \gamma - \sin \alpha \sin \beta] x_e \\
&\quad + [\cos \alpha \sin \gamma + \sin \alpha \cos \beta] y_e - \cos \beta \sin \gamma z_e, \\
y_j &= -[\sin \alpha \cos \gamma + \cos \alpha \sin \beta] x_e \\
&\quad - [\sin \alpha \cos \beta \sin \gamma + \sin \alpha \cos \beta \cos \gamma] y_e + \sin \beta \cos \gamma] z_e, \\
z_j &= \sin \beta \cos \gamma x_e + \sin \beta \sin \gamma y_e + \cos \beta z_e.
\end{align*}
\]
and

\[ x_c = \sin \theta \cos \phi , \]
\[ y_c = \sin \theta \cos \phi , \]
\[ z_c = \cos \theta , \]  \hspace{1cm} (3.1.16) \]

where \( \theta_j \) and \( \phi_j \) are the polar angles of the EFG principal axes with respect to the magnetic field at the site \( j \). By the use of \( z_j^2 \) and \( x_j^2 - y_j^2 \), the first and the second order quadrupole interactions are expressed by

\[ \omega_{Q}^{(1)}_j = \frac{e^2qQ}{8I(2I-1)} (3z_j^2-1+7x_j^2-y_j^2) , \]  \hspace{1cm} (3.1.17) \]
\[ \omega_{Q}^{(2)}_j = \frac{(e^2qQ/h)^2}{192\omega_0} \{(9(1-z_j^2)^2-6\eta(1+z_j^2)(x_j^2-y_j^2)) +4\eta^2z_j^2+\eta^2(x_j^2-y_j^2)^2 \]
\[ -72z_j^2(1-z_j^2)-48\eta z_j^2(x_j^2-y_j^2) \]
\[ -8\eta^2(1-z_j^2)+8\eta^2(x_j^2-y_j^2)^2 \} . \]  \hspace{1cm} (3.1.18) \]

Then the calculation must be performed over the ranges \( 0 < \theta < \pi \), and \( -\pi < \phi \leq \pi \) in order to accomplish the powder averaging.

In the actual calculation, \( \cos \theta \) is used instead of \( \theta \) because the powder averaging (3.1.10) can be rewritten as

\[ f(t_2,t_1) = \int d\phi \int d(\cos \theta) S(t_2,t_1) . \]  \hspace{1cm} (3.1.19) \]

Thus the region of the integration is divided into \( N \) with respect to \( \cos \theta \) \( (-1 < \cos \theta < 1) \) and \( \phi \) \( (-\pi < \phi \leq \pi) \).

In the case where only one kind of site exists, one can tentatively coincide the crystalline frame with the EFG
principal axes. Since $S(t_2, t_1)$ is symmetric with respect to $\cos \theta$ and $\phi$, the number of calculation can be reduced by a factor of 4 of the total division.

3.1.3 Line Broadening

The line broadening effect should be incorporated as the multiplication of the FID's Eq. (3.1.19) by the Gaussian (or Lorentzian) function. Since the origin of the line broadening is mainly due to dipole interaction in the detection period but the distribution of (static) quadrupole interaction and/or dipole interaction cause the line broadening in the evolution period, the broadening factors in each period may be different, and in practice they are used as adjustable parameters. Other reasons which bring about the line broadening are discussed later.

3.1.4 2D Fourier transformation

The FID's obtained by the above procedure should be Fourier-transformed to deduce the 2-dimensional spectrum.

$$g(\omega_2, \omega_1) = \int \exp(-i\omega_2 t_2) dt_2 \int \exp(-i\omega_1 t_1) dt_1 f(t_2, t_1),$$

(3.1.20)

where $f(t_2, t_1)$ is given in Eq. (3.1.19).
3.2 Computational Procedure

Two simulation programs were constructed, one for the simulation of 2D nutation spectrum without chemical exchange and the other with chemical exchange.

Brief explanation of the former is given in the following. Although the analytical expression has been given, the diagonalization is performed numerically so as to be able to treat the general case in which spin $1 \leq 3/2$.

1) Parameter Input

Input the parameters necessary to simulate the spectrum.
- spin number
- Larmor frequency
- quadrupole coupling constant and asymmetry parameter
- rf pulse strength in the frequency unit
- number of experiments and increment of the pulse length
- number of sampling points and sampling interval
- number of division over the sphere for numerical integration

2) Quadrupole Interaction

The first and the second order quadrupole interactions are determined at a given angle $\theta$ and $\phi$ with respect to the external magnetic field.

3) Calculation of the FID

Diagonalize the Hamiltonian and calculate the evolution of the density matrix to evaluate the FID signal. These are accumulated in the range $0 \leq \cos \theta < 1$, and $0 \leq \phi < \pi$. 

-41-
Short explanation of the simulation program with chemical exchange is given below.

1) Parameter Input

Input the parameters necessary to calculate the FID's.
Larmor frequency
number of site for exchange
\( e^2 q Q / h \), \( \eta \) and the Euler angles
which relate the crystalline frame
and the principal axes of the EFG at each site
relative population of each site
chemical exchange rate between any pair of the sites
rf pulse strength in the frequency unit
number of experiments and increment of the pulse length
number of sampling points and sampling interval
number of division over the sphere for numerical integration

2) Quadrupole interaction at a given orientation

The first and the second order quadrupole interactions
are calculated at a given angle \( \theta \) and \( \phi \) with respect to the external magnetic field.

3) Calculation of FID

Diagonalize the Liouvillians corresponding to each dimension and calculate the FID.

These are summed over the sphere in the range
\(-1 < \cos \theta < 1 \) and \(-\pi < \phi \leq \pi \).

In each case, the number of divisions over the sphere is chosen to be sufficient to produce the powder spectrum, i.e., 3000-10000. A set of data points \( 128 \times 256 \) are used to calculate the FID's. The program lists are given in
Appendix. The program is coded in FORTRAN and calculated by the ACOS-6 of the computer center of Osaka University and/or NEC PC-9801E/VM personal computer.

The Fourier transformation (Eq. (3.1.20)) was done by the use of the ASPECT-3000 minicomputer incorporated in the BRUKER MSL-200 NMR system. The ASPECT-3000 is equipped with an array processor which can execute the 2D Fourier transformation very efficiently and with the plotting routine to draw up the spectrum. The data conversion program provided by BRUKER Co. Ltd. was modified to convert the data format between the MS-DOS operating system on NEC PC-9801 personal computer and the ASPECT-3000 system. The line broadening parameters can also be defined in the ASPECT-3000 system.
References

[1] R. Janssen and W.S. Veeman,

    in *Electron Spin Relaxation in Liquids*,

[3] See, for example,
    U. Haeberlen,
    *High Resolution NMR in Solids*,
4. Sample

4.1. NaN0₂ and NaHgCl₃·2H₂O

NaN0₂ crystallizes in an orthorhombic (space group Im2m) crystal system with the unit cell dimension of \( a = 3.569 \text{ Å} \), \( b = 5.563 \text{ Å} \), and \( c = 5.384 \text{ Å} \). \( Z = 2 \). [11]

Crystal of NaHgCl₃·2H₂O is orthorhombic (space group Pnma) with four molecules in the unit cell [2]. The lattice parameters are: \( a = 9.372 \text{ Å} \), \( b = 4.037 \text{ Å} \), and \( c = 18.71 \text{ Å} \). Sodium atoms are coordinated by two H₂O molecules and four chlorine atoms.

Both of the above compounds have only one kind of sodium site and can be used to preliminary test of 2D nutation NMR method.

4.2 Na₂SeO₃

This crystal has three nonequivalent sodium sites [3]. This sample can be used to examine whether 2D nutation NMR method can be applied to determine the quadrupole interaction parameters at each site.

4.3. Naₓ₋ₓZrₓSi₁₋ₓP₂₋ₓO₁₂

The system Naₓ₋ₓZrₓSi₁₋ₓP₂₋ₓO₁₂ has been known to be a fast alkali-ion conductor. [4] The crystal structure is shown in Fig. 4.1. [5] Complete solid solution exists for the composition between \( x = 0 \) and 3 and the crystal structure varies between R3 \((0.0 \leq x < 1.8, 2.2 < x \leq 3.0)\) and C2/c \((1.8 \leq x \leq 2.2)\). The latter is a slightly deformed structure of the former. The structure consists of a three-dimensional skeletal network of PO₄ (and/or SiO₄) tetrahedra which are corner-shared with ZrO₆ octahedra. The ZrO₆ octahedron is linked by three PO₄ tetrahedra so as to form a ribbon along the hexagonal c-axis and also linked by six PO₄
Figure 4.1
Crystal structure of \( \text{Na}_{1+x} \text{Zr}_2 \text{Si}_x \text{P}_{3-x} \text{O}_{12} \).
tetrahedra to form a two-dimensional sheet in the c-plane. This has two kinds of sodium sites named 1 and 2. In the case $x=0$ (NaZr$_2$P$_3$O$_{12}$), sodium occupies the site 1 (Na$^{(1)}$) only which is an octahedral site surrounded by six oxygen atoms of ZrO$_6$, and the site 2 remains unoccupied. As $x$ increases, the population of the site 2 (Na$^{(2)}$) increases. Na$^{(1)}$ lies on the three-fold axis and is also surrounded by six Na$^{(2)}$ sites which locate in the same plane of the nearest-neighbor O$^{2-}$. Thus it has been supposed that the sodium ion transport occurs through the path Na$^{(1)}$→Na$^{(2)}$→Na$^{(1)}$. The conductivity changes with $x$ and assumes the maximum value at $x=2.0$, but the activation energy for conduction is almost constant in the range between $x=0.0$ and 3.0.

The compound can therefore be an appropriate model for examining the sodium ion exchange by NMR. Moreover, since the site symmetries at the Na$^{(1)}$ and Na$^{(2)}$ sites are both lower than the cubic symmetry and so non-zero quadrupole interaction in each site is expected to exist. Therefore the application of the new theory for the 2D nutation NMR on chemically exchanging system to Na$_{1+x}$Zr$_2$Si$_x$P$_{3-x}$O$_{12}$ brings about information on the dynamic process and the microscopic mechanism of the ion conduction in this material.
References

[1] R.W.G. Wyckoff,  
*Crystal Structures*, 2nd Ed., Vol. 2,  
John Wiley & Sons, 1964

*Crystal Structures*, 2nd Ed., Vol. 3,  
John Wiley & Sons, 1965


[5] H.Y-P. Hong,  
5. Experiment
5.1. Sample Preparation
5.1.1. NaN\textsubscript{2}O and NaHgCl\textsubscript{3}·2H\textsubscript{2}O

NaN\textsubscript{2}O is of commercial source (Nacalai Tesque, guaranteed reagent grade, purity 98.0%) and used without further purification.

NaHgCl\textsubscript{3}·2H\textsubscript{2}O was prepared from aqueous solution of the appropriate mixture of NaCl (Tomita Seiyaku) and HgCl\textsubscript{2} (Nacalai Tesque, guaranteed reagent grade, purity 99.5%). Colorless polycrystals were grown by slow evaporation of water. The X-ray powder diffraction pattern of this product (Fig. 5.1) was compared with that calculated with the lattice parameters given in the literature [1]. The result identified NaHgCl\textsubscript{3}·2H\textsubscript{2}O but indicated at once the existence of small amount of HgCl\textsubscript{2}. However, this HgCl\textsubscript{2} impurity is supposed to have little influence on the NMR of \textsuperscript{23}Na.

5.1.2. Na\textsubscript{2}SeO\textsubscript{3}

Na\textsubscript{2}SeO\textsubscript{3} was prepared from aqueous solution of a stoichiometric mixture of NaOH (Nacalai Tesque, reagent grade, purity 93%) and selenious acid H\textsubscript{2}SeO\textsubscript{3}. H\textsubscript{2}SeO\textsubscript{3} is prepared by dissolving SeO\textsubscript{2} (Nacalai Tesque, guaranteed reagent grade, purity 98%) in water. Slow evaporation of the solution gave the white powder.

5.1.3. Na\textsubscript{1-x}Zr\textsubscript{2}Si\textsubscript{x}P\textsubscript{3-x}O\textsubscript{12}

The powdered specimen was synthesized from the stoichiometric mixture of Na\textsubscript{2}CO\textsubscript{3} : ZrO\textsubscript{2} : SiO\textsubscript{2} : NH\textsubscript{4}H\textsubscript{2}PO\textsubscript{4} = 1+x : 4 : 2x : 2(3-x), x=0.0, 1.0, and 2.0. [2] The reagents used here were : Na\textsubscript{2}CO\textsubscript{3}, Nacalai Tesque, guaranteed reagent grade, purity 99.5%; ZrO\textsubscript{2}, Nacalai Tesque, reagent grade;
The X-ray powder diffraction pattern of NaHgCl₃·2H₂O.
SiO$_2$, Nacalai Tesque, guaranteed reagent grade; NH$_4$H$_2$PO$_4$, Wako Junyaku, guaranteed reagent grade, purity 98%. The mixture was at first heated to 900°C for several hours to decompose Na$_2$CO$_3$ and NH$_4$H$_2$PO$_4$, then heated to 1200°C for 10 to 20 hours in the platinum crucible in an electric furnace. The sample obtained here is white fine powders. The specimen was identified by X-ray powder diffraction.
Figure 5.2
The X-ray powder diffraction pattern of NaZr$_2$Si$_3$O$_{12}$. 

-52-
Figure 5.3
The X-ray powder diffraction pattern of Na$_3$Zr$_2$SiP$_2$O$_{12}$. 

-53-
5.2 Nutation NMR

The $^{23}$Na NMR spectrum was measured by the use of the BRUKER MSL-200 NMR system at the Larmor frequency of 52.938 MHz. In some cases, offset of $\pm 10$ kHz was added so as to minimize the difference between the resonance frequency and the rf frequency. The pulse length was increased from 1 to 128 $\mu$s every 1 $\mu$s, or from 2 to 256 $\mu$s every 2 $\mu$s by the use of the automation program. The FID signal was sampled every 0.8 $\mu$s. The number of data points was usually 1k words. Each FID was quadrature-detected and accumulated 16 to 500 times using phase cycling technique to eliminate phase and intensity errors arising from the non-ideality of the pulses and/or the receivers in each experiment. The recycle time for accumulation was set to be greater than the time required for the magnetization recovery towards thermal equilibrium value; Usually it was 5 s. The temperature of the sample was controlled using VT-1000 temperature control system which is equipped in the MSL-200 system and measured by the Cu-Constantan thermocouples. The fluctuation of the temperature is within $\pm 1$ K.

In order to minimize the effect of the rf pulse inhomogeneity, the samples were sealed in the glass ampules with 10mmφ in ca. 10mm long. The signal of sodium from the ampule was negligible since the glass ampule used here was very thin and the amount of sodium in it was negligibly small compared with that in the sample.

The data acquired were 2D Fourier transformed by the use of ASPECT-3000 computer. Before 2D FT, zero filling up to 1k or 2k words in the $F_1$ dimension was made in order to increase the digital resolution of the spectrum. In some
cases, the trapezoidal function was multiplied to the $F_1$ data to avoid the effect of cut-off of the tail that causes auxiliary wiggles on either side of the spectrum [4].
References

[1] R.W.G. Wyckoff,
Crystal Structures, 2nd Ed., Vol. 3.
John Wiley & Sons, 1965


[4] L-O. Hagman and P. Kierkegaard,

[5] T.C. Farrar and E.D. Becker,

A.G. Marshall and F.R. Verdun,
6. Data Analysis

6.1 Nutation Spectrum

Figs. 6.1 and 6.2 show stacked and contour plots of typical 2D nutation spectrum simulated with parameters $e^2Qq/h = 0.2$ MHz, $\eta = 0$, and $\omega_1/2\pi = 50$ kHz. The horizontal axis, which will be called $F_2$ for brevity, is the conventional 1D NMR spectrum axis and the projection onto this axis gives the powder spectrum characterized by the second order quadrupole interaction. (See Fig. 6.2a.) The vertical axis, $F_1$, shows the nutation spectrum whose pattern varies with strength of the quadrupole interaction relative to the rf strength.

If the Hamiltonian in the evolution period, $H_2$, does not contain any useful information other than quadrupole interaction, an FT over $t_1$ gives nutation spectrum which gives rise directly to the ratio $\Omega_0/\omega_1 = [3e^2Qq/2I(2I-1)\hbar^3]/\omega_1$, where $\Omega_0$ is the lowest pure quadrupole resonance frequency.

Fig. 6.3 illustrates the simulated dependence of the nutation spectrum on the strength of the quadrupole interaction for $I = 3/2$ ($\eta = 0$ and $\omega_1/2\pi = 50$ kHz). The numbers on the right-hand side of the spectrum represent $e^2Qq/h$. The bottom spectrum corresponds to the case when the quadrupole interaction is absent; only one sharp peak appears at around $\omega_1$ as mentioned in Sec. 2.3. As the strength of the quadrupole interaction is increased, the spectrum splits into several peaks and they move away from $\omega_1$. In the topmost spectrum, the quadrupole interaction is so strong that only one peak is found at around $2\omega_1$. In this case, the intensity of the peak at $2\omega_1$ is reduced to 1/4 of that of the peak at $\omega_1$ in the case of $e^2Qq/h = 0$, indicating that
Figure 6.1
Stacked plot of 2D nutation spectrum simulated with parameters $e^2 Q q / h = 0.2$ MHz, $\eta = 0$, $\omega_1 / 2\pi = 50$ kHz.
Figure 6.2
Contour plot of simulated 2D nutation spectrum. Calculated parameters are as in Fig. 6.1. a) Projections onto F₁ and b) F₂ axis, respectively.
only the transition between \( m = \pm 1/2 \) can be excited by weak rf field.

The variation of the nutation spectrum with \( \eta \) is shown in Fig. 6.4 for \( \Omega_0/\omega_1 = 2.0 \). When \( \eta \neq 0 \), the spectrum splits into several peaks and their separations increase with increasing \( \eta \). If \( \eta = 1 \), they are merged with each other.

Based on the above results, one can determine the quadrupole interaction parameters from the positions and (relative) intensities of the peaks. In order to avoid possible effect of improper phase setting in the experiment on the spectrum, only the magnitude spectra are used to compare the experimental nutation spectra with the theoretical ones, although it gives rather broad peaks owing to the contribution of the dispersion component.

The magnitude spectrum means

\[
\sqrt{\text{A}(\omega)^2 + \text{D}(\omega)^2},
\]

where A and D are absorption (real) and dispersion (imaginary) components of the spectrum.
Figure 6.3
Dependence of nutation spectrum on the strength of quadrupole interaction.
Figure 6.4

$\eta$ dependence of nutation spectrum. $\Omega_0/\omega_1 = 2$. 
6.2 Data Analysis

1) NaN0₂ and NaHgCl₃.2H₂O

The 2D nutation spectrum of NaN0₂ is shown in Fig. 6.5, and its projection onto the \( F_1 \) axis is shown in Fig. 6.6a. Three broad peaks are found at near 0, \( \omega_1 \), and \( 2\omega_1 \). The peak at around 0 is probably due to the offset effect which is caused by a non-zero offset between the Larmor frequency and the rf frequency and/or due to the rf inhomogeneity. This point will be discussed further in Sec. 7.2. If this minor disagreement is ignored, the nutation spectrum can be interpreted with \( e^2Qq/h \approx 1.1 \text{ MHz} \) which has been reported in the literature [1]. The projection onto the \( F_2 \) axis (Fig. 6.6b) gives the structure due to the second order quadrupole interaction, and \( \eta \) can be estimated from its line shape to be \( \approx 0.1 \).

The spectrum of NaHgCl₃.2H₂O is shown in Fig. 6.7, which resembles with that of NaN0₂, but the relative intensities of the peaks are different (See Fig. 6.8). This spectrum corresponds to the spectrum of \( e^2Qq/h \approx 0.6 \text{ MHz} \) and \( \eta \approx 0.2 \).

2) Na₂SeO₃

This sample has three nonequivalent sodium sites and these can be distinguished in the nutation spectrum in Fig. 6.9: The slices of the spectrum at the positions marked by arrows (Figs. 6.10a-c) are different from each other in their relative intensities of the peak near \( \omega_1 \) and that near \( \omega_1 \), due certainly to the presence of three different quadrupole interactions. The strength of the quadrupole interaction at the sites a, b, and c is estimated to be 1.4, 0.8, and 1.3 MHz, respectively. The value \( \eta \) is estimated to be 0.8 and 0.0 for a and b. No significant temperature
Figure 6.5
Contour plot of 2D nutation spectrum of NaNO₂ at room temperature.
Figure 6.6
2D nutation spectrum of NaNO₂ at room temperature.
a) Projection onto F₁ axis. b) Projection onto F₂ axis.
Figure 6.7
Contour plot of 2D nutation spectrum of NaHgCl₃·2H₂O at room temperature.
Figure 6.8
2D nutation spectrum of NaHgCl₆.2H₂O. Projection onto F₁ axis.
Figure 6.9
Contour plot of 2D nutation spectrum of Na₂SeO₃ at room temperature.
Figure 6.10
The slices of the spectrum at the positions marked by arrows in Fig. 6.9.
dependence was found except at the highest temperature (330 K), at which a sharp peak appeared at $\omega_1$. This peak corresponds obviously to very small quadrupole interaction but the origin of such small $e^2Qq/h$ is not clear.

4) $\text{Na}_{1-x}\text{Zr}_2\text{Si}_3\text{-xP}_x\text{O}_{12}$

The spectra of the samples with $x = 0.0$ and 1.0 have shown no significant temperature dependence.

The spectrum for $x = 0.0$ at room temperature is shown in Fig. 6.11. In the spectrum of $x = 0.0$, one can clearly distinguish two sites (i.e., a considerable amount of fraction of sodium ions occupies the 'site 2').

Remarkable temperature dependence of the spectrum is found for $x = 2.0$. The temperature dependence of 1D spectrum is shown in Fig. 6.12 and that of 2D nutation spectrum is shown in Figs. 6.13-6.17. By Fig. 6.12 alone, one can neither distinguish two nonequivalent sites nor assign the nature of motion that causes the variation of the lineshape. But the analysis of 2D nutation spectrum can provide fruitful information about these points.

In the spectrum of the lowest temperature (116 K), it is shown clearly that there are two independent nonequivalent sodium sites and so it can be assumed that the chemical exchange between the sites does not occur. The slices at the position indicated by arrows are shown in Figs. 6.18a and b. These were compared with the simulated patterns with $e^2Qq/h$ of 1.0 MHz and 1.5 MHz, respectively. Moreover from the relative intensities of the two spectral components, the spectrum in Fig. 6.18a ($e^2Qq/h = 1.0$ MHz) was assigned to the site 1 and Fig. 6.18b ($e^2Qq/h = 1.5$ MHz) to the site 2. The projection onto $F_2$ axis (except the spectral component
Figure 6.11
Contour plot of 2D nutation spectrum of NaZr$_2$Si$_3$O$_{12}$ at room temperature.
Figure 6.12
Temperature dependence of 1D spectrum of Na$_3$Zr$_2$SiP$_2$O$_{12}$. 
Figure 6.13
Contour plot of 2D nutation spectrum of Na$_2$Zr$_2$SiP$_2$O$_7$ at 116 K.
Figure 6.14
Contour plot of 2D nutation spectrum of Na₃Zr₂SiP₂O₁₂ at 186 K.
Figure 6.15

Contour plot of 2D nutation spectrum of Na₃Zr₂SiP₂O₁₂ at 237 K.
Figure 6.16
Contour plot of 2D nutation spectrum of Na₃Zr₂SiP₂O₁₂ at 300 K.
Figure 6.17
Contour plot of 2D nutation spectrum of Na₃Zr₂SiP₂O₁₂ at 363 K.
Figure 6.18

The slices at the positions marked by the arrows in Fig. 6.13.
Figure 6.19

Projection onto F_2 axis of 2D nutation spectrum of Na_3Zr_2SiP_2O_12 at 116K.
appeared at around 0 frequency in the F_1 dimension) is shown in Fig. 6.19. Using the above values of e^2Qq/h the simulation of the best fitting to the experimental line shape was obtained by putting \( \eta = 0.0 \) (site 1) and 0.8 (site 2), and that difference between the chemical shifts at the two sites is 16 kHz. These results are supported by the crystal data: The site 1 has three fold symmetry and so \( \eta \) should be 0.

As the temperature was increased, the difference between the two sites became gradually unclear, and it disappeared to give a spectrum which corresponded to well defined one site case at the highest temperature (Fig. 6.17, 363 K). This phenomenon suggests strongly that the rapid chemical exchange occurs between the two nonequivalent sites at the high temperature.

The simulation of the spectrum at the highest temperature led to the values of the apparent interaction parameters \( e^2Qq/h = 1.1 \) MHz and \( \eta = 1.0 \) (see Fig. 6.20). These parameters as well as the above values for the rigid lattice were used to estimate the Euler angles between the two EFG tensors to be \( \beta = 30.0 \), \( \gamma = 60.0 \). The simulation of the spectrum at each temperature was performed to reproduce the experimental spectrum with the chemical exchange rate \( k \) as unknown parameter. The simulated spectra are shown in Figs. 6.21-6.25. It was found that the chemical exchange rates are 0.1 kHz at 237 K, 1 kHz at 300 K, and 10 kHz at 363 K. From these values the activation energy for the chemical exchange between the sites 1 and 2 was estimated to be \( E_a \approx 13 \) kJ/mol. On the other hand the activation energy values obtained above do not coincide with that found in the conductivity measurement (\( E_a \approx 31 \) kJ/mol) [2]. The large
Figure 6.20
Projection onto $F_1$ axis of 2D nutation spectrum of $\text{Na}_3\text{Zr}_2\text{SiP}_2\text{O}_{12}$ at 363K.
Figure 6.21

Contour plot of 2D nutation spectrum simulated with chemical exchange rate $k = 0.001 \, \text{kHz}$. Other parameters are described in the text.
Figure 6.22
Contour plot of 2D nutation spectrum simulated with chemical exchange rate $k = 0.01$ kHz.
Figure 6.23

Contour plot of 2D nutation spectrum simulated with chemical exchange rate $k = 0.1 \text{ kHz}$. 
Figure 6.24
Contour plot of 2D nutation spectrum simulated with chemical exchange rate $k = 1.0$ kHz.
Figure 6.25

Contour plot of 2D nutation spectrum simulated with chemical exchange rate $k = 10 \text{ kHz}$.
discrepancy between the $E_a$'s values obtained by the NMR and conductivity measurement suggests that there exists a fundamental difference between the local motion of the sodium ions and the global motion which causes the net ionic conduction. This point will be discussed later.
References


7. Discussion

7.1 Summary of the Present Work

So far in the previous Chapters a new theoretical method to describe the evolution of the quadrupolar spin system under the influence of strong rf field was established. This method is based on the Liouville representation and is superior in the following points to the other methods previously developed:

1. It is easy to construct the theoretical expression for the complex interaction between the spin system and the rf field and so can be easily extended to the system with spin higher than 3/2.

2. Although the dimension of the matrix to be determined is far larger than that based on other standard methods, the formalism with the Liouvillian can be coded by computer language(s) and therefore is much suitable for the computation by a big computer.

3. Liouville representation has a form which can incorporate effects other than spin interaction in a straightforward manner. This property makes it possible to apply the nutation method to chemically exchanging system.

The new method was coded by FORTRAN to prepare the general simulation program which is necessary for analyzing the experimental 2D nutation spectra. The program can be applied to quadrupolar nuclei with spin numbers 3/2 to 9/2 and to systems with and without chemical exchange.

The 2D nutation NMR experiments were conducted for $^{23}$Na species involved in several compounds:

1. The $^{23}$Na resonances in NaNO$_2$ and NaHgCl$_3$.2H$_2$O were used to establish the optimal experimental conditions for the 2D
nutation spectra and to evaluate the sensitivity of the spectra to the quadrupole interaction parameters, \( e^2Qq/h \) and \( \eta \).

2. The \(^{23}\text{Na}\) nutation NMR was applied to \( \text{Na}_2\text{SeO}_3 \) to distinguish the three crystallographically nonequivalent Na sites in this compound. The value \( e^2Qq/h \) at the individual sites could be determined and also \( \eta \) was estimated for two of the three sites in this material.

3. The \(^{23}\text{Na}\) 2D nutation NMR was used to examine the dynamic process of \( \text{Na}_{1-x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12} \). The spectrum was remarkably temperature dependent and by applying the new theoretical method for the chemically exchanging system to it the chemical exchange rate of Na ions between two nonequivalent sites was estimated at each temperature. It was found that the activation energy deduced from the nutation spectra differs significantly from that determined by a previous conductivity measurement.

In the course of this work a number of problems have been encountered concerning the practice of the 2D nutation NMR. In what follows I will discuss the applicability, advantage and/or disadvantage of the 2D nutation NMR newly developed in the present work.
7.2 2D Nutation NMR

Nuclear quadrupole interaction can provide a lot of useful information on the static and dynamic structures of crystalline materials. In the case that $e^2Qq/h$ is larger than about 1 MHz, the pure quadrupole resonance can be applied to determine the quadrupole interaction parameters. When $e^2Qq/h$ is much smaller than $\sim 100$ kHz, the conventional NMR is used to detect the quadrupole-perturbed spectra either on single crystal or powdered specimen.

Many of chemically interesting nuclei such as $^{23}$Na, $^{27}$Al, $^{39}$K, $^{59}$Co, etc. give often $e^2Qq/h$ of the magnitude between ca. 100 kHz and a few MHz region. In such a frequency region it is extremely difficult to apply the above two methods because of the limitation on the sensitivity and/or band width of the radio-frequency spectrometers. Moreover when a number of crystallographically nonequivalent sites exist for the nuclei of interest, it is usually almost impossible to analyze the complex spectra even if the second order quadrupole interaction could be detected.

It was shown in a preceding Chapter that the 2D nutation NMR can successfully be applied to such cases. Since the strength of the rf pulse usually available is 100 kHz at most, it means that this method can be applied to determine the quadrupole coupling constant $\Omega_0/2\pi$ up to about 1 MHz.

Most remarkable feature of the nutation NMR method lies in the fact that if a strong rf field can be used and if the condition $H_0, H_0 S \ll H_r$ holds, undesirable line broadening effect due to $H_0$ and $H_0 S$ along the $F_1$ axis is dramatically reduced. (In the usual 1D spectrum which corresponds to the $F_2$ direction, the line broadening due to other interactions
can not be eliminated.) In this way, detailed information on the quadrupole interaction can be derived from the nutation spectrum.

Another advantage of the nutation NMR is found in its simple setting of the experiment as having been demonstrated in Chap. 5.

A special use of the nutation method is, as pointed out [1], the determination of relative orientation between the EFG and the other interaction tensors. It is possible if the dominant interaction in the detection period, $t_2$, is other than the second order quadrupole interaction. For example, if the static magnetic field is considerably high the line width due to the chemical shift extends over wide frequency range and may dominate the second order quadrupole interaction. In such case, the spectra developed onto $F_1$ and $F_2$ axes contain the information mainly on the quadrupole and chemical shift interaction, respectively, and the correlation between them allows to determine the angles between tensors of both interactions.

However, several effects are found to deform the spectrum. These are discussed below. 

a) Peak near 0 in $F_1$

When an off-resonant rf pulse is applied, i.e. when Larmor frequency in the absence of quadrupole interaction does not coincide with the rf frequency, there must appear a peak at zero frequency. This can be explained as follows in the case of $I = 1/2$ for simplicity. If the offset between the rf frequency and the Larmor frequency is $\Delta \omega$, the signal at the end of the pulse becomes
\[ S(t) = [\alpha(1 - \cos 2\omega t) + i\beta \sin 2\omega t] \]  

(7.2.1)

where

\[ \Omega = \sqrt{\Delta \omega^2 + \omega_1^2} \]
\[ \alpha = \frac{\omega_1 \Delta \omega}{\Omega^2} \]
\[ \beta = \frac{\omega_1}{2\Omega} \]  

(7.2.2)

Since \( \Delta \omega \neq 0 \), \( \alpha \) does not vanish and the term independent of time generates the peak at 0 frequency. Also the cosine term survives and this results in the phase modulation along \( F_1 \) which will cause the distortion of the spectrum. Then it is desirable to minimize the resonance offset as long as possible. But when the inhomogeneity of the external magnetic field and/or dipole interaction between the spins are significant, this effect cannot be eliminated perfectly.

Another cause of central peak is the effect of the second order quadrupole shift during the evolution period which has been neglected in the theoretical formulation. The nutation spectrum including these effects is shown in Fig. 7.1. The greater the quadrupole interaction, the greater the intensity of the central peak.

b) Line Broadening

Another undesirable effect in the nutation NMR is caused by the inhomogeneity of the rf field in space. This cannot be avoided in the use of the solenoid of the finite length. The rf magnetic field is strongest at the middle of the coil and decreases to some extent at the ends of it. [2] This brings about the distribution of the ratio \( \Omega_0 \)/\( \omega_1 \) and it causes the line broadening in \( F_1 \) dimension. Also, if the shape of the rf pulse is not rectangular (although it is
Figure 7.1
Dependence of nutation spectrum on the ratio $\Omega_2/\omega_1$ including the second order quadrupole interaction as well as chemical shift.
assumed tacitly), it causes the spectrum to modify. The effect of the inhomogeneity in the rf field cannot be treated quantitatively.

In the discussions so far, the effect of the relaxation was not taken into account, but in the actual experiment the relaxation of the spin system sometimes influences the spectrum. The qualitative analysis of the Bloch equation shows that the magnetization which nutates around the rf field is decreased with the time constant \( T_n = 2/(1/T_1 + 1/T_2) \) under the assumption that \( \omega_1 \gg 1/T_1, 1/T_2 \). This leads to the conclusion that the inverse of the peak width along \( F_1 \) cannot exceed \( 2T_2 \) and the best resolution is determined by \( T_2 \) since usually \( T_2 \) is much shorter than \( T_1 \) in solids. When the effect of the relaxation can be treated theoretically, it must give the information on the dynamics of the nucleus. The relaxation effect on the nutation spectrum has been examined by the rotary echo nutation method [3] in which the effect of homogeneous line broadening arising from the relaxation can be separated from that of inhomogeneous line broadening due to the distribution of the quadrupole interaction and/or external magnetic field.

c) \( T_1 \) noise

Another relaxation effect which influences the spectrum is \( T_1 \) noise [4] which is due to the variations of the experimental conditions from experiment to experiment in a 2D sequence, leading to irregular fluctuations of the signal as a function of \( t_1 \). In the 2D nutation NMR, \( T_1 \) noise is caused if the recycle time between the accumulation is too short for the magnetization to recover towards the thermal equilibrium value, \( M_0 \). Since the magnetization recovery

-95-
depends on \( t_1 \) (and the recycle time) the peaks at \( 2\omega_1, 3\omega_1, \ldots \) appears in the nutation spectrum.
7.3 Chemical Exchange Effect

As already demonstrated in a previous Chapter, the 2D nutation NMR gives its full ability in the situation where the spectrum arises from several nonequivalent sites. Often the signals corresponding to them overlap with each other and it is very difficult to decide which peak corresponds to each site. While by the use of 2D nutation NMR one can easily distinguish each site according to the difference of the strength of quadrupole interaction.

It was shown theoretically and experimentally that the nutation spectrum is drastically changed when the chemical exchange of the resonant nuclear species is excited. The detailed analysis of the spectrum brings about the quantitative information of the mechanism of the chemical exchange. Especially when slow and fast limits of the spectra can be obtained, one can determine the relative orientation of the EFG tensors as well as the rate constant of the exchange. Thus the method can be used to examine the mechanism of chemical exchange, ionic conduction, and/or solid state reaction from the microscopic point of view.

In Chap. 6 it was pointed out for Na$_{1+x}$Zr$_2$Si$_x$P$_{3-x}$O$_{12}$ that the activation energy for the sodium exchange was estimated from the 2D nutation NMR experiment to be 13 kJ/mol and that this value was very small compared with 31 kJ/mol deduced from a previous conductivity measurement. The most simple model for ionic conduction is based on the classical hopping mechanism through successive nearest-neighbor sites. In such a model conductivity measurement and NMR should give the same activation energy and jump rate. Serious discrepancies as was found above are often
encountered. [5] In the case that the ion transport occurs through the hopping between two or more nonequivalent ionic sites as was found in Na$_{1+x}$Zr$_2$Si$_x$P$_3$-$x$O$_{12}$, the discrepancy between the activation energies determined by different techniques can qualitatively interpreted. Consider an ion transport through a potential shown in Fig. 7.2. As the potentials at sites 1 and 2 are largely different one ion can jump easily from 'site 2' to 'site 1' but the opposite is much difficult. If the neighboring 'site 1' is initially occupied, the ion will hop back and forth between the nearest sites until one of the other 'site 1' happens to become empty. The repetition of such local motion does not contribute to the net conductivity whereas it affects the NMR spectrum. The exchange and conduction of the sodium ions in Na$_{1+x}$Zr$_2$Si$_x$P$_3$-$x$O$_{12}$ are considered to apply to such a model. The 2D nutation NMR method looks at the rapid local motion with an average activation energy while the ion transport experiment measures an energy which is the sum of the activation energy for the jump and the energy for the vacancy formation at the 'site 1'. This idea enables one also to interpret the experimental results that the activation energy obtained from conductivity measurement is independent of the composition (x) while that from NMR is strongly dependent on x. (When x = 2 the frequent jump between the sites 1 and 2 was observed as mentioned before but no sodium jump was recognized in the specimens with x = 0 and 2. In the latter two samples the activation energies for the sodium exchange appear to be infinity.)
Figure 7.2
Nonequivalent site model with deep and shallow wells.
References


A. Samoson and E. Lippmaa.


   Principles of Nuclear Magnetic Resonance

   Physics of Superionic Conductors, Chap. 6.
$NOTRUNCATE

$DECLARE

PROGRAM NUTATION

C

COMPLEX*16 ARYDAT(1,1024), HI(100), RI(100), RDR(100)

COMPLEX*16 EI(10), EE(10), REC(10), ERC(10), W(10)

REAL*8 THD(10), QCC, ETA, QC2, WI, WIF(10)

REAL*8 A1, AO, P12, TI(2), CT1, CT2(20000), CPI(900), HI1(2,100), S, D

INTEGER*4 DIM(2), MXD(2), NSP, NT, NP, MXT, I, J, K, L, N, ERS

CHARACTER*15 RGF, TOF

C

EQUIVALENCE (HI, HI1), (CT2(901), CPI(1))

COMMON /ARYDAT/ARYDAT,DIM

COMMON /PARAMS/THD,QCC, ETA, QC2, QIF, WIF

COMMON /WKVAR/RDR, EE, REC, ERC, W

C

Declarations of Constants

PARAMETER(P12=6.283185307179586D+00)

DATA MXD/1024,1/

C

Spin Number

WRITE(*,'(A11Y)') 'Spin #2 = '

READ(*,'(I2)') NSP

S=DBLE(NSP)/2.0D+00

A1=S*S+S

C

Lamor Frequency

WRITE(*,'(A20Y)') 'Lamor Freq / MHz = '

READ (*,'(F7.4)') W0

C

Quadrupole Interaction Parameters

WRITE(*,'(A17Y)') '0eqQ / MHz, = '

READ (*,'(2F10.6)') QCC, ETA

C

RF Strength in Frequency Units

WRITE(*,'(A27Y)') 'ORF Field Strength / kHz = '

READ (*,'(F6.3)') W1

C

Sampling Points in each Dimension

DO 300 I=1,2

WRITE(*,'(A13,1I)') 'Dimension : , I

WRITE(*,'(A35,14,ASY)')

& ' Number of Sampling Points ( Max. ,MXD(1), ) = '

READ (*,'(I5)') DIM(I)

WRITE(*,'(A25Y)') 'Time increment / us = '

READ (*,'(F5.3)') TI(I)

300 CONTINUE
C RGF : Stores Computational Conditions
C TDF : Saves FID Data
C
C 0REGISTRY File Name = 'RGF'
C 0TIME Domain File Name = 'TDF'
C
C Get the Number to be calculated
C
C Number of Division over 0
C
C Max. : 20000 (η = 0) 900 (η > 0) = '
C
DO 400 I=1,NT
   CT1= DBLE(I)/DBLE(NT)
   CT2(I)= CT1*CT1
400 CONTINUE
IF (ETA .EQ. 0.00+00) THEN
   NP=1
   CPI(I)=0.00+00
ELSE
   NP=NT
   DO 410 I=1,NP
      CPI(I)= ETA*OCOS(P12*DBLE(I)/DBLE(NT))
410 CONTINUE
END IF

C Store the Parameters
C
OPEN (UNIT=50, FILE=RGF, ACCESS= 'SEQUENTIAL')
WRITE(50, '(A40)') ' Computational Conditions ------ '
WRITE(50, '(A16)') ' Interactions '
WRITE(50, '(A2, F8.3)') ' Lamor Freq / MHz = ', W0
WRITE(50, '(A22, F7.3)') ' RF Field / kHz = ', W1
WRITE(50, '(A15, F10.6, A8, F10.6)')
& ' QCC / MHz = ', QCC, ': ETA = ', ETA
WRITE(50, '(A15)') ' Calculation '
WRITE(50, '(A44)') ' Dimension Data Points Time IncremenLs'
DO 500 I=1,2
500 CONTINUE
WRITE(50, '(7X, I1, 10X, 14, 9X, F10.5)') I, DIM(I), TI(I)
WRITE(50, '(A28)') ' Total Division over Θ = ', NT
WRITE(50, '(A42, A15)') ' Data Stored in ', TDF
CLOSE (UNIT=50)
Determine the Parameters suitable to Calculation

QCC=QCC/DBLE(NSP*NSP)*2.5D-01
QCC=QCC/W0*PI2*TI(2)*(AI-7.5D-01)
W1=PI*PI2*TI(1)*1.0D-03
D=DBLE(NSP)/2.0D+00
DO 600 I=1,NSP+1
DO 710 J=1,NT
DO 710 J=1,NT
WRITE(*,'(A38,15/)') & Total Division over THETA, PHI = ',NT*NP
WRITE(*,'(A30,15/)') Powder Averaging Start here
DO 710 J=1,NT
WRITE(*,'(A30,15/)') Powder Averaging Now : ',I*NP
WRITE(10,FMT=9000)
CONTINUE
CONTINUE
CLOSE (UNIT=10)
FORMAT(D22.16,1X,D22.16)
Normal End.
Error Exist in the Procedure.
WRITE(*,'(A18,15/)') 'File Write Error ',ERS
GO TO 99999
WRITE(*,'(A23,15/)') 'Diagonalization Error ',ERS
END
SUBROUTINE EVOLVE(J, M, H1, RI, E1, CT2, CT1, ERR)
Calculate the Evolution of the Density Vectors

COMPLEX*16 ARYDAT(4+024), HI(L,L), RI(L,L), EI(L), IC, Q2E
COMPLEX*16 RDR(10,10), EE(10), REC(10), ERC(10), W(10)
REAL*8 H11(2,L,L), Q1, Q2, D, CT2, CT4, ST2, ST4, CP1, CP2, SP2
REAL*8 THD(10), QC, ETA, QC2, QIF(10), WIF(10)
INTEGER*4 DIM(2), N1, N2, J, K, ERR

COMMON /ARYDAT/ARYDAT,DIM
COMMON /PARAMS/THD,QC,ETA,QC2,QIF,WIF
COMMON /WRKVAR/RDR,EE,REC,ERC,W

Transformation of Coordinate to Molecular Frame

CT4 = CT2 * CT2
ST2 = 1.0D+00 - CT2
ST4 = ST2 * ST2
CP2 = CP1 * CP1
SP2 = ETA * ETA - CP2

First Order Quadrupole Splitting
Q1 = QC * (3.0D+00 + CT2 - 1.0D+00 + ST2 * CP1)

Second Order Quadrupole Shift for the Central Transition
Q2 = QC2 * (ST4 * 9.0 - (1.0 - CT4) * CP1 * 6.0 + (CT2 * 4.0 + ST4) * CP2 + CT2 * SP2 * 4.0
& (-ST2 * (CT2 * (9.0 + CP1 * 6.0 + CP2) + SP2) * 8.0)
Q2E = DCMPLX(DCOS(Q2), DSNJN(Q2))

Set the Hamiltonian

DO 30 I=1,L
DO 20 J=1,L
H1(J,J) = 0.0D+00
20 CONTINUE
H11(2,1,1) = QIF(1)
IF ( (.GT. 1) H11(2,1-1,1) = WIF(1-1)
192 IF ( (.LT. L) H11(2,1+1,1) = WIF(1) )
30 CONTINUE
Get the Eigenvalues and Eigenvectors to Calculate Exponentials

CALL CHEQRD(L,HI,E1,R1,ERR)
IF (ERR .NE. 0) RETURN
DO 100 I=1,L
EE(I)=CDEXP(E1(I))
100 CONTINUE
DO 110 J=1,L
DO 110 I=1,L
RDR(I,J)=0.0D+00
110 CONTINUE
DO 120 I=1,L
RDR(I,J)=RDR(I,J)+RI(K,1)*THD(K)*RI(K,J)
120 CONTINUE
DO 200 I=1,L
REC(I)=RI(L/2,1)
ERC(I)=RI(L/2+1,1)
200 CONTINUE
DO 210 I=1,L
W(I)=0.0D+00
DO 210 J=1,L
W(I)=W(I)*REC(J)*RDR(J,1)
210 CONTINUE
DO 220 I=1,L
1C=0.0D+00
DO 220 J=1,L
1C=1C+W(J)*ERC(J)
220 CONTINUE
DO 300 N2=1,DIM(2)
ARYDAT(N2,N1)=ARYDAT(N2,N1)+1C
300 CONTINUE
RETURN
END
SUBROUTINE CHEGQRD(N,L,C,EC,VC,ERR)
   C  Calculate the Eigenvalues and Eigenvectors of Symmetric Matrix
   C
   COMPLEX*16 LC(N,N),VC(N,N),EC(N),ZX,ZY,ZZ,ZR,ZC,ZS
   REAL*8  CDABSP,DEL
   INTEGER*4 I,J,IP1,LL,LU,ITR,ITRMAX,ERR
   
   CDABSP(ZZ)=DABS(DREAL(ZZ))+DABS(DIMAG(ZZ))
   DATA DEL,ITRMAX/5.0D-15,30/
   
   C  Set the Eigenvectors to Unit Matrix
   DO 110 I=1,N
      DO 100 J=1,N
         VC(J,I)=0.0D+00
      100 CONTINUE
      VC(1,1)=1.0D+00
   110 CONTINUE
   
   C  Search for a Small Sub-diagonal Element.
   C
   LU=N
   300 ITR=0
   310 LL=LU
   320 IF (CDABSP(LL.LL-1) .GT. DEL) THEN
      LL=LL-1
   325 IF (LL .GT. 1) GO TO 320
   326 END IF
   327 IF (LL .NE. LU) THEN
      C  If Convergence is not Attained within 30 Iterations, 
      C  Truncate the Computation.
      C
      IF (ITR .GT. ITRMAX) GO TO 10000
      C
   329 C  Determine the Origin Shift as the Eigenvalue of the 2 by 2
   330 C  Bottom Submatrix which is Nearer to the bottom Element.
   331 C
   332 ZX=(LL.LL-1)L+LC(LL,LU-1)+LC(LL,LU-1)*0.5D+00
   333 ZZ=CDABSP(ZY-ZZ)+CDABSP(ZY+ZZ)*ZZ+ZX
   334 LC(LL.LL)=LC(LL.LL)-ZZ
   335 ZC=1.0D+00
Left- and Right-hand Transformation.

DO 360 I=LL,LU-1
   IP1=I+1
   ZX=LC(I,1)
   ZY=LC(IP1,1)
   ZR=CDSQRT(ZX*ZX+ZY*ZY)
   IF (CDABSP(ZR).LT. DEL) GOTO 20000
   LC(1,1)=ZN*ZR
   IF (1,.GT. LL) LC(1,1-1)=ZS*ZR
   LC(IP1,1P1)=LC(IP1,1P1)-ZS
   ZC=ZX/ZR
   ZS=ZY/ZR
   DO 330 J=1P1,N
      ZY=LC(J,1)
      LC(1,J)=ZY*ZC+LC(IP1,J)*ZS
      LC(IP1,J)=LC(IP1,J)*ZC-ZY*ZS
   CONTINUE
   DO 340 J=1,N
      ZY=VC(J,1)
      LC(J,1)=ZY*ZC+VC(J,1P1)*ZS
      LC(J,1P1)=VC(J,1P1)*ZC-ZY*ZS
   CONTINUE
   LC(LU,LU-1)=LC(LU,LU)*ZS
   LC(LU,LU)=LC(LU,LU)*ZC+ZS
   ITR=ITR+1
   GO TO 310
END IF

QR-Transformation is Over.
Eigenvalues are Given
by the Diagonal Elements of the Resultant Matrix.

DO 400 I=1,N
EC(I)=LC(1,1)
CONTINUE
Microsoft FORTRAN Optimizing Compiler Version 4.01

330 C
331 C Normal Exit.
332 C
333 C ERR=0
334 C RETURN
335 C
336 C Error Exit.
337 C 10000 : Not Converged.
338 C 20000 : Devide by Zero.
339 C
340 10000 ERR=10000
341 RETURN
342 20000 ERR=20000
343 RETURN
344 END
`$DECLARE
PROGRAM EXCHANGE
Simulation Program for 2D Nutation NMR with Chemical Exchange

COMPLEX*8 ARD(256,128)
REAL*8 QCC(2), ETA(2), QC2(2), ET2(2), CHS(2), RFS, EXC(2,2,2)
REAL*8 ALP(2), BET(2), GAM(2), TDX(8), THD(4,2), R(4), P(2)
REAL*8 X(-50:50.0:50), Y(-50:50.0:50), Z(-50:50)
REAL*8 SA(2), CA(2), SB(2), CB(2), SG(2), CG(2), TI(2)
REAL*8 W0, W1, D, PID, SNT, D2R, P11, P12, SQ3
INTEGER*4 DIM(2), MXD(2), NSP, NSI, MXS, NN, MXT, I, J, N, ERS
CHARACTER*15 CHA, CHA

EQUIVALENCE (TDX, THD), (CHA, RGF)
COMMON /ARD/ARD, DIM, TDX, R, P
COMMON /PAR/QCC, ETA, QC2, ET2, CHS, RFS, EXC
COMMON /ARG/SA, CA, SB, CB, SG, CG

PARAMETER(NSP=4, MXS=2, MXT=50)
PARAMETER(D2R=1.745329251994329D-02, SQ3=8.660254037844385D-01)
PARAMETER(PI1=3.141592653589793D+00, PI2=6.283185307179586D+00)
DATA MXD/128, 256/

Lamor Frequency
READ (*,'(A20)') 'OLamor Freq / MHz = '
WRITE(*,'(F7.4)') W0

Number of Sites to be Considered
READ (*,'(I1)') NSI
IF (NSI .GT. MXS) GOTO 1

Quadrupole Interaction Parameters and Chemical Shifts
DO 100 I=1,NSI
WRITE(*,'(A9)') 'Site : ', I
WRITE(*,'(A21)') ' cgQ / MHz, eta = '
READ (*,'(2F10.6)') QCC(I), ETA(I)
WRITE(*,'(A37)') ' Eular Angles of Principal Axis = '
WRITE(*,'(3F10.6)') ALP(I), BET(I), GAM(I)
D=ALP(I)*D2R
SA(I)=DSIN(D)
CA(I)=DCOS(D)
D=BET(I)*D2R
SB(I)=DSIN(D)
CB(I)=DCOS(D)
D=GAM(I)*D2R
SG(I)=DSIN(D)
CG(I)=DCOS(D)
WRITE(*,'(A27)') ' Chemical Shift / kHz = '}

READ (*,'(F10.6)') CHS(I)
CHS(I)=CHS(I)*1.0D-03
59 100 CONTINUE
60 C Chemical Exchange
61 C
62 WRITE(*,'(A80,'(A3))') 'Null Equilibrium Population of Each Site are Equal (Y or N) ?'
63 READ(*,'(A1)') CHA
64 & (ICHAR(CHA).EQ.ICHAR('Y')).OR.
65 IF ((ICHAR(CHA).EQ.ICHAR('Y'))) THEN
66 D=DBLE(NSI)
67 DO 200 I=1,NSI
68 P(I)=1.0D+00/D
69 200 CONTINUE
70 ELSE
71 D=0.0D+00
72 DO 210 I=1,NSI
73 WRITE(*,'(A38)') 'Null Relative Population of Site ',I,' = '  
74 READ(*,'(F6.4)') P(I)
75 D=D+P(I)
76 210 CONTINUE
77 DO 220 I=1,NSI
78 P(I)=P(I)/D
79 220 CONTINUE
80 ELSE
81 DO 230 I=1,NSI
82 EXC(I,1,1)=0.0D+00
83 DO 230 J=1,NSI
84 IF (J.GT.1) THEN
85 WRITE(*,'(A30,I11,1X,A3)') 'Exchange Rate from ',I,' to ',J,' / MHz = '  
86 READ(*,'(F10.8)') EXC(J,I,1)
87 EXC(I,J,1)=EXC(J,I,1)*P(I)/P(J)
88 END IF
89 IF (I.NE.J) EXC(I,1,1)=EXC(I,1,1)-EXC(J,1,1)
90 230 CONTINUE
91 C RF Strength in Frequency Units
92 C
93 WRITE(*,'(A29)') 'RF Field Strength / kHz = '  
94 READ(*,'(F5.3)') W1
95 C
96 DIM(1),DIM(2) : Sampling Points in each Dimension
97 C
98 DO 300 I=1,2
99 WRITE(*,'(A38)') 'Dimension : ',I
100 2 WRITE(*,'(A30Y)') 'Number of Sampling Points = '
101 READ(*,'(I5)') DIM(I)
102 IF (DIM(I).GT.MXD(I)) THEN
103 WRITE(*,'(A14)') 'O Too Large !! '
104 GO TO 2
105 END IF
106 WRITE(*,'(A35)') 'Time increment ( in microsec ) = '
107 READ(*,'(F5.3)') TI(I)
108 300 CONTINUE
109 C RGF : Stores Computational Condition
110 C TDF : Saves FID Data
Line# | Source Line |
--- | --- |
117 | C WRITE(*,'(A25Y)') '0Registry File Name = ' |
118 | READ(*,'(A15)') RGF |
119 | WRITE(*,'(A25Y)') ' Time Domain File Name = ' |
120 | READ(*,'(A15)') TDF |
121 | C Get the Number to be calculated |
122 | 3 WRITE(*,'(A33Y)') 'NumberOf Division over THETA = ' |
123 | READ(*,'(I1)') N |
124 | IF (N.GT. MXT) GOTO 3 |
125 | DO 400 I=O, N |
126 | Z(I)=DBLE(I)/D |
127 | SNT=DSQRT(1.0-Z(I)*Z(I)) |
128 | DO 400 J=O, N |
129 | X(J,I)=SNT*COS(PID*DBLE(J)) |
130 | Y(J,I)=SNT*SIN(PID*DBLE(J)) |
131 | X(-J,I)=X(J,I) |
132 | Y(-J,I)=Y(J,I) |
133 | 400 CONTINUE |
134 | WRITE(*,'(A38,15/)') |
135 | & Total Division over THETA, PHI = ',N*N*4-N*2 |
136 | C Store the Parameters |
137 | OPEN (UNIT=50, FILE=RGF, ACCESS='SEQUENTIAL') |
138 | WRITE(50,'(A40)') ' ----- Computational Conditions ----- ' |
139 | WRITE(50,'(A17)') ' < Interactions >' |
140 | WRITE(50,'(A22,F8.3)') ' Lamor Freq / MHz = ', W0 |
141 | WRITE(50,'(A22,F7.3)') ' RF Field / kHz = ', WI |
142 | DO 500 I=1,NSI |
143 | WRITE(50,'(/A10,11,A16,F10.8,A2)') |
144 | & Site : ',I,' ( Population = ',P(I),')' |
145 | & WRITE(50,'(A16,F6.4,A8,F6.4)') |
146 | & QCC / MHz = ',QCC(I)', ETA = ',ETA(I) |
147 | & WRITE(50,'(A19,F5.2,A2,F5.2,A2,F5.2)') |
148 | & Euler Angles : ',ALP(I)', BET(I)', GAM(I) |
149 | & Chemical Shift / kHz = ',CHS(I)*1.0D+03 |
150 | 500 CONTINUE |
151 | WRITE(50,'(/A25)') ' < Exchange Rates / MHz >' |
152 | DO 510 I=1,NSI |
153 | WRITE(50,'(/A25)') ' Dimension Data Points Time Increments' |
154 | DO 530 I=1,2 |
155 | WRITE(50,'(8X,11,10X,13,10X,F10.5)') I,DIM(I),TI(I) |
156 | 510 CONTINUE |
157 | WRITE(50,'(/A16)') ' < Calculation >' |
158 | WRITE(50,'(A45)') ' Total Division = ',N*N*4-N*2 |
159 | WRITE(50,'(/A19,A15)') ' Data Stored in ',TDF |
160 | CLOSE (UNIT=50) |
161 | C Symmetrize the Exchange Matrix
DO 600 I=1,NSI
   THD(1,I)= SQ3*P(I)
   THD(2,I)=-P(I)
   THD(3,I)= 0.0D+00
   THD(4,I)=-SQ3*P(I)
600 CONTINUE

DO 610 I=1,NSI
   IF (J .NE. I) EXC(J,I,1)=EXC(J,1,1)*P(I)/P(J)
610 CONTINUE

DO 620 I=1,NSI
   QCC(1)=P12*QCC(1)/QCC(1)/W0*Ti(2)/9.6D+01
   TCC(1)=P12*QCC(1)/8.0D+00*Ti(1)
   ETA(1)=ETA(1)*ETA(1)
   CHS(1)=P12*CHS(1)/Ti(2)
   DO 620 J=1,NSI
   EXC(J,1,2)=EXC(J,1,1)*Ti(2)
   EXC(J,1,1)=EXC(J,1,1)*Ti(1)
620 CONTINUE

RFS=P12*W1*Ti(1)+1.0D-03

DO 710 I=-N+1,N-1
   WRITE(*,'(A30,15)') 'Powder Averaging Now : ',NN*N*2
   DO 710 J=-N+1,N
   NN=NN+1
   CALL EVOLVE(NSP,NSI,X(J,IABS(I)),Y(J,IABS(I)),Z(I),ERS)
   IF (ERS .NE. 0) GOTO 20000
710 CONTINUE

CLOSE (UNIT=10)

OPEN(UNIT=10,FILE=TDF)

WRITE(10,'(E13.7,1X,E13.7)',IOSTAT=ERS,ERR=10000) ARD(J,1,D)

CLOSE (UNIT=10)

GO TO 99999

WRITE(*,'(A18,15)') 'File Write Error ',ERS
GO TO 99999
233 200000 WRITE(*,'(A23,15)') ' Diagonalization Error ' ERR
234 C
235 99999 END
236 C
237 BLOCK DATA IXT01Z
238 COMPLEX*8 ARD(256,128)
239 REAL*8 TDX(8),R(4),P(2)
240 INTEGER*4 DIM(2)
241 COMMON /ARD/ARD,DIM,TDX,R,P
242 C
243 C Transformation Laws in lx to lz basis
244 C
245 DATA R/ 6.123724356957945D-01,
246 & 3.53553905832738D-01,
247 & -1.060860171779821D+00,
248 & -6.123724356957945D-01/
249 END
250 $PAGE
SUBROUTINE EVOLVE(L,M,X,Y,Z,ERR)

Calculate the Evolution of the Density Vectors

COMPLEX*8 ARD(256,128)
COMPLEX*16 L1(8,8),L1(4,2,4,2),Q1(8,8),E1(8),L2(2,2),Q2(2,2),E2(2)
COMPLEX*16 DZ(2,128),RQ1(2,8),PQ2(2,2),Y
REAL*8 E1(2),E2(2),CHS(2),RFS,EXC(2,2,2)
REAL*8 X,Y,Z,SA(2),CA(2),SB(2),CB(2),SG(2),CG(2)
REAL*8 XC(4,4,2),WQ1,WQ2,WQ3,WQ4,X2,Y2,Z2,CT2,ST2,CP1
REAL*8 TDX(8),R(4),P(2),CDABSP,EPS
INTEGER*4 DIM(2),I,J,K,S1,S2,SS,LM,ERR

EQUIVALENCE (L1,HI)
PARAMETER(SQ3=8.660254037844385D-01)
COMMON /P^R/QCC,ET^,QC2,ET2,CHS,RFS,EXC
COMMON /ARG/SA,CA,SB,CB,SG,CG
AD/ARD,DIM,TDX,R,P
CDABSP(C)=DABS(DREAL(C))**DABS(DIMAG(C))
DATA EPS/L.0D-18/

DO 100 S=1,M

transformation of coordinate to molecular frame

Z2=SB(S)**CG(S)**X*SB(S)**SG(S)**Y*CB(S)**Z
X2=-(CA(S)**CB(S)**SG(S)**X)**SA(S)**SG(S)**X

&
Y2=-(CA(S)**CB(S)**SG(S)**Y)**CA(S)**SG(S)**X

&
(1.0D+00-(T2**2+Z2**2))

&
CP1=(X2*Y2-Z2**2)*ETA(S)

First order quadrupole splitting

WQ1=QCC(S)**(CT2**2+Z2**2)*CP1

Second order quadrupole shift + chemical shift

WQ2=CHS(S)+QC2(S)

&
*L2(S,S)=DCMPLX(EXC(S,S),WQ2)

Set the hamiltonian in the basis X

WQ3=WQ1*SQ3
X(1,1,S)= WQ1+RFS
X(1,2,S)= WQ3
X(1,3,S)= WQ3
X(1,4,S)= 0.0
X(2,2,S)= -RFS
X(2,3,S)= 0.0
X(2,4,S)= WQ3
X(3,3,S)= RFS*3.0D+00
X(3,4,S)= WQ3
XC(4,4,5) = -WQ1*RFS

C Set the Liouvillan

DO 220 S=1,M
   DO 200 I=1,L
      H1(I,S,1,S) = DCMPLX(EXC(S,S,1),XC(I,1,S))
   DO 200 J=1+1,L
      H1(I,S,J,S) = DCMPLX(0.00+00, XC(I,J,S))
   H1(J,S,1,S) = H1(J,S,J,S)
   200 CONTINUE
   DO 210 SS=S+1,M
      DO 210 J=1,L
         IF (I.EQ. J) THEN
            H1(I,S,1,SS) = EXC(1,SS,1)
            H1(I,SS,1,S) = EXC(1,SS,1)
         ELSE
            H1(I,S,J,SS) = 0.00+00
            H1(J,S,1,SS) = 0.00+00
            H1(I,SS,J,S) = 0.00+00
            H1(J,SS,1,S) = 0.00+00
         END IF
      END
      210 CONTINUE
   220 CONTINUE

C Get the Eigenvalues and Eigenvectors to Calculate Exponentials

LM = 1
CALL CHEQRD(LM,L1,1,E1,Q1,ERR)
IF (ERR .NE. 0) RETURN
DO 400 I=1,LM
   E1(I) = CDEXP(E1(I))
   400 CONTINUE
   SS = 0
   DO 420 S=1,2
      DO 410 K=1,LM
         RQ1(S,K) = 0.00+00
      DO 410 J=1,S
         DO 410 I=1,LM
            RQ1(S,K) = RQ1(S,K) + R(J)*Q1(J,SS,K)*Q1(I,K)*TDX(I)
      410 CONTINUE
   420 CONTINUE
   Call CHEQRD(M,L2,1,E2,Q2,ERR)
   IF (ERR .NE. 0) RETURN
   DO 500 I=1,M
      E2(I) = CDEXP(E2(I))
   500 CONTINUE
   DO 510 S2=1,M
      DO 510 S1=1,M
DO 510 S = 1, M

PQ2(S1, S2) = PQ2(S1, S2) + D(S1) * Q2(S1, S2) * Q2(S, S2)

CONTINUE

510 DO 600 1 = 1, DIM(1)

DO 600 S = 1, M

CONTINUE

Calculate Density Vectors at the end of rf Pulse

DO 600 1 = 1, DIM(1)

CONTINUE

Calculate FID's

CONTINUE

700 ARD(J, 1) = ARD(J, 1) + PQ2(S1, S2) * DZ1(S2, 1)

CONTINUE

710 CONTINUE

RETURN

END
SUBROUTINE CHEQRD(N,LC,NDW,LC,VC,ERR)

Calculate the Eigenvalues and Eigenvectors of Symmetric Matrix

REAL*8 LC(N,N),VC(N,N),EC(N),ZX,ZY,ZZ,ZR,ZQ,ZC,ZZ

INTEGER*4 I,J,K,IPM,IML,JPM,JMI,LL,LU,M,ITR,ITRMAX,ERR

CDABS(P,Z)=DABS(DREAL(ZZ))+DABS(DIMAG(ZZ))

DATA DEL,ITRMAX/1.0D-15,30/

Parameter Error Check

IF ((N .LE. 1) .OR. (NDW .GT. N)) GO TO 20000

Set the Eigenvectors to Unit Matrix and Determines the Band Width of the Matrix under Treatment.

DO 110 I=1,N
   DO 100 J=1,N
      VC(J,I)=0.0D+00
      CONTINUE
      VC(1,I)=1.0D+00
      CONTINUE
      DO 100 J=1,N
         CONTINUE
      END IF

Reduction of Band Width to Tridiagonal Matrix by Jacobi Rotations.

DO 270 M=NDW,2,-1
   DO 260 I=1,N-M
      IPM=I+M
      IM1=1-IPM
      IF (CDABS(LPZC(1,IPM)) .GT. DEL) THEN
         ZR=-LC(1,IM1)/LC(I,IPM)
         ZQ=CDSQRT(1.0D+00+ZR*ZR)
         IF (CDABS(ZQ) .LT. DEL) GOTO 30000
         ZS=1.0D+00/ZQ
         ZC=-ZS*ZR
         DO 250 J=1,N
            ZZ=LC(IPM,J)
            ZZ=LC(IPM,J)*ZZ+LC(I,IPM)*ZS
            CONTINUE
         END IF
      CONTINUE
      DO 250 J=1,N
         ZZ=LC(J,1IM1)
         LC(J,1IM1)=ZZ+LC(J,1IPM)*ZS
         LC(J,1IPM)=LC(J,1IPM)*ZC-ZZ*ZS
      CONTINUE
   CONTINUE
   DO 250 J=1,N
      ZZ=VC(J,1IM1)
      CONTINUE
   DO 250 J=1,N
      ZZ=VC(J,1IM1)
      CONTINUE
   GOTO 270
   CONTINUE
   END

END
LINE 10
09-27-90
19:36:47

Microsoft FORTRAN Optimizing Compiler Version 4.01

457 VC(J, J+M) = VC(J+M, J) * ZS
458 V C(J, J+M) = V C(J+M, J) * ZS
459 CONTINUE
460 DO 260 J = M+1, N
461 JPM = J+M
462 JM1 = JPM + 1
463 IF (CDABSP(LC(J, JM1)) .GT. DEL) THEN
464 ZR = -LC(J, JPM) / LC(J, JM1)
465 ZQ = CDASRT(1.0D0 + ZR * ZR)
466 IF (CDABSP(ZQ) .LT. DEL) GOTO 30000
467 ZS = 1.0D0 / ZQ
468 ZC = -ZS * ZR
469 DO 230 K = 1, N
470 ZZ = LC(JPM, K)
471 LC(JPM, K) = ZZ * ZC + LC(JM1, K) * ZS
472 LC(JM1, K) = LC(JM1, K) * ZC - ZZ * ZS
473 CONTINUE
474 DO 240 K = 1, N
475 ZZ = LC(K, JPM)
476 LC(K, JPM) = ZZ * ZC + LC(K, JM1) * ZS
477 LC(K, JM1) = LC(K, JM1) * ZC - ZZ * ZS
478 CONTINUE
479 DO 250 K = 1, N
480 ZZ = VC(K, J+M)
481 VC(K, J+M) = ZZ * ZC + VC(K, JM1) * ZS
482 VC(K, JM1) = VC(K, JM1) * ZC - ZZ * ZS
483 CONTINUE
484 END IF
485 CONTINUE
486 CONTINUE
487 CONTINUE
488 C Search for a Small Sub-diagonal Element.
489 C
490 C
491 LU = N
492 300 ITR = 0
493 310 LL = LU
494 320 IF (CDABSP(LC(LL, LL-1)) .GT. DEL) THEN
495 LL = LL - 1
496 IF (LL .GT. 1) GO TO 320
497 END IF
498 IF (LL .NE. LU) THEN
499 C If Convergence is not Attained within 30 Iterations, Truncate the Computation.
500 C
501 C
502 C
503 IF (ITR .GT. ITRMAX) GO TO 10000
504 C Determine the Origin Shift as the Eigenvalue of the 2 by 2 Bottom Submatrix which is Nearer to the bottom Element.
505 C
506 C
507 C
508 ZX = (LC(LL, LL-1) + LC(LU, LL)) * 0.5D0 + 00
509 ZY = ZX - LC(LU, LL)
510 ZZ = CDASRT((LC(LL-1, LL) + LC(LU, LL-1) + ZY * ZY)
511 ZZ = DSIGN(1.0D0, CDABSP(ZY - ZZ) - CDABSP(ZY + ZZ)) * ZZ + ZY
512 LC(LL, LL) = LC(LL, LL) - ZZ
513 ZC = 1.0D0 + 00
514 DO 360 I = LL, LU - 1
IP1 = 1 + 1

Left- and Right-hand Transformation.

ZX = LC(1, 1)
ZY = LC(IP1, 1)
ZR = CD_SQRT(ZX*ZX + ZY*ZY)
IF (CDABS(ZR) .LT. DEL) GO TO 30000
LC(1,1) = ZC*ZR
IF (I .GT. LL) LC(1,1-1) = ZS*ZR
LC(IP1, IP1) = LC(IP1, IP1) - ZZ
ZC = ZX/ZR
ZS = ZY/ZR
DO 330 J = IP1, N
    ZY = LC(J, 1)
    LC(J, 1) = ZY*ZC + LC(J, IP1) * ZS
    CONTINUE
330 DO 340 J = 1, I
    ZY = LC(J, 1)
    LC(J, 1) = ZY*ZC + LC(J, IP1) * ZS
    CONTINUE
340 CONTINUE
LC(1, 1) = LC(1, 1) + ZZ
DO 350 J = 1, N
    VC(J, 1) = ZY*ZC + VC(J, IP1) * ZS
    CONTINUE
350 CONTINUE
L(LU, LU-1) = L(LU, LU) * ZS
CONTINUE
END IF
LU = LU - 1
IF (LU .GT. 1) GO TO 300
QR-Transformation is Over.
Eigenvalues are Given by the Diagonal Elements of the Resultant Matrix.

DO 400 I = 1, N
EC(1) = LC(1, 1)
CONTINUE
END

Normal Exit.

ERR = 0
RETURN

Error Exit.

10000 : Not Converged.
20000 : Parameter Error.
30000 : Devide by Zero.

ERR = 10000
RETURN
Line# Source Line
573 20000 ERR=20000
574 RETURN
575 30000 ERR=30000
576 RETURN
577 END

Global Symbols

Name          | Class | Type | Size | Offset
---            | ---   | ---  | ---  | ---
Code size     | 0000  | (0)  | 0000 | (0)
Data size     | 0000  | (0)  | 0000 | (0)
Bss size      | 0000  | (0)  | 0000 | (0)

No errors detected