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Solid State Chemical Exchange

in Some Sodium Salts as Studied by 2D Nutation NMR

By Hiroshi Ohki

SOLID STATE CHEMICAL EXCHANGE IN SOME SODIUM SALTS

AS STUDIED BY 2D NUTATION NMR

BY

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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 $3/2 \sim 9/2$ and to systems with and without chemical exchange.

The 2D nutation NMR experiments were conducted for ²³Na in several compounds. The ²³Na resonance in NaNO₂ and in NaHgCl₃.2H₂O 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, e²Qq/h, and the asymmetry parameter, η , of the electric field gradient at the site of the resonant nucleus.

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The ²³Na 2D nutation NMR was applied to Na₂SeO₃ to distinguish the three crystallographically nonequivalent Na sites in this compound. The quadrupole coupling constants at the individual sites could be determined and also η was estimated for two of the three sites in this material.

Na1+x Zr2Six P3-x O12 has been known as a typical sodium ion conductor. The ²³Na 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.

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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 guadrupole 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^2Qq/h) and the asymmetry parameter of the electric field gradient (η). If the e²Qq/h is consider-

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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 guadrupole 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-

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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 NaNO₂ 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, Na_{1+x}Zr₂Si_xP_{3-x}O₁₂, 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 ρ obeys the von Neumann equation of motion [2]

$$d\rho/dt = -i[H,\rho]$$
, (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 :

$$d\boldsymbol{\rho}/dt = -iL\boldsymbol{\rho} , \qquad (2.1.2)$$

where p is the density superkets in the column form, i.e.,

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$$\boldsymbol{\rho} = {}^{t} \left(\rho_{11} \ \rho_{12} \ \rho_{13} \ \dots \ \rho_{1n} \ \rho_{21} \ \dots \ \rho_{nn} \right) ,$$
(2.1.3)

where n = 2I+1 and I is the spin. L is defined through the relation

$$L = H \otimes E - E \otimes {}^{t}H , \qquad (2.1.4)$$

where E is the unit operator which has the same dimension as H, and ^tH represents the transposed matrix of H and \otimes stands for the direct product [3] 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 :

$$L^{d} = U^{-1}LU$$

= $(U^{-1} \otimes U^{-1})(H \otimes E - E \otimes {}^{t}H)(U \otimes U)$
= $H^{d} \otimes E - E \otimes H^{d}$, (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

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in the interaction representation which removes unnecessary term H_{\emptyset} from the Hamiltonian. In this case, the Liouvillian can be written

	- T -	(2 1 7)
L = L0	+ L1 ,	(2.1.7)

where

Le	Ξ	Hø	8	Е	-	Е	⊗ ^t Hø	,	(2.1.8a)
L1	=	H1	8	Е	-	Е	\otimes ^t H ₁		(2.1.8b)

Then the Liouville description of the interaction representation is expressed by

þ.	=	$exp(+iLet)\rho$,	(2.1.9)

$$L^{*} = \exp(+iL_{\theta}t)L_{1}\exp(-iL_{\theta}t) , \qquad (2.1.10)$$

where ρ and L are density superkets and Liouvillian in the interaction representation, respectively. Accordingly the equation of motion of the density superkets becomes

$$d\rho'/dt = -iL'\rho$$
 (2.1.11)

If the Liouvillian L' is explicitly time-independent, Eq. (2.1.11) can be solved formally :

$$\rho'(t) = \exp(-iL't)\rho(0)$$
 (2.1.12)

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

$$M_x = Tr(I_x \rho)$$
, (2.1.13)

while in the Liouville formalism,

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$M_{\times} = I_{\times} \rho ,$

(2.1.14)

where I_x 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

 $A \times B = \begin{pmatrix} a_{11}B & a_{12}B & \dots & a_{1n}B \\ a_{21}B & a_{22}B & \dots & a_{2n}B \\ & & & \ddots & \ddots \\ & & & \ddots & & \ddots \\ a_{n1}B & a_{n2}B & \dots & a_{nn}B \end{pmatrix}$

Thus the resultant matrix has n² 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 $I \ge 1$ consist generally of 21+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

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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 halfinteger 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 |m₂ > 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-

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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

H1	=	Hz	+	H _Q (Ω)	+	HD	+	Hc s	+	Hrr(t),	(2.2.1)
Ha	=	Hz	+	$H_{0}(\Omega)$	+	Hn	+	Hes			(2.2.2)

where H_Z is the Zeeman interaction, H_0 the quadrupole interaction, H_0 the dipole interaction, H_{CS} represents the chemical shift, and $H_{r,f}$ is the coupling between the spin and the applied rf field. Ω represents the angle between the external static magnetic field and principal axes of EFG tensor. Their explicit forms are [2]

$H_z = \omega_0 I_z$	
= $\gamma H_{\theta} I_z$,	(2.2.3)
$H_{\Theta}(\Omega) = \sum Q_m V_{-m}$,	(2.2.4a)
$Q_8 = a[3I_2^2 - I(1+1)]/2$,	
$Q_{\pm 1} = \sqrt{6a[I_z I_{\pm} + I_{\pm} I_z]/4} ,$	
$Q_{\pm 2} = \sqrt{6aI_{\pm}^2/4}$,	
$V_8 = V_{ZZ}/2$,	
$V_{\pm 1} = (V_{Z \times \pm i} V_{Z \times }) / \sqrt{6}$,	
$V_{\pm 2} = (V_{X \times} - V_{Y Y} \pm 2iV_{X Y})/2\sqrt{6}$,	
a = eQ/[I(2I-1)],	(2.2.4b)
$H_D = \Sigma I_i DI_j$,	(2.2.5)
$Hcs = H\sigma I$.	(2.2.6)

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 $H_{rf} = \omega_1 \left[I_X \cos(\omega_0 t) + i I_Y \sin(\omega_0 t) \right] , \qquad (2.2.7)$

where ω_0 is the nuclear Larmor frequency, D and σ are the dipole interaction and the chemical shift tensors, respectively, and ω_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 $H_Z \gg H_0 \simeq H_{rf}$ >>H_D, H_{CS}. This situation is realized in the case of nuclei with fairly large quadrupole interaction such as ²³Na, ³⁹K, ⁵⁹Co, ⁹³Nb 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

$$H_{Q}' = H_{Q}^{(1)} + H_{Q}^{(2)}$$
, (2.2.8)

where

 $H_{Q}^{(1)} = e^{2}qQ/8I(2I-1)(3\cos^{2}\theta - 1 + \eta\sin^{2}\theta\cos 2\phi) \times [3I_{2}^{2} - I(I+1)]$ = $\omega_{Q}[I_{2}^{2} - I(I+1)/3]$, (2.2.9)

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and

$$\begin{split} H_{Q}^{(2)} &= (3e^{2}qQ/2I(2I-1))^{2}I_{z}/32\omega_{\theta} \\ &\times [\{9(1-\cos^{2}\theta)^{2}-6\eta(1-\cos^{4}\theta)\cos 2\phi \\ &+ \eta^{2}(1+\cos^{2}\theta)^{2}\cos 2\phi + 4\eta^{2}\cos^{2}\theta(1-\cos^{2}2\phi)\} \\ &\times [2I_{z}^{2}-2I(I+1)+1] \\ &- \{9(1-\cos^{2}\theta)\cos^{2}\theta + 6\eta(1-\cos^{2}\theta)\cos^{2}\theta\cos 2\phi \\ &+ \eta^{2}(1-\cos^{2}\theta)\cos^{2}\theta\cos^{2}2\phi \\ &+ \eta^{2}(1-\cos^{2}\theta)(1-\cos^{2}2\phi)\} \\ &\times 4[8I_{z}^{2}-4I(I+1)+1]] , \quad (2.2.10) \end{split}$$

where, θ and ϕ 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

$$Hcs' = \sigma Iz$$
.

(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

$$H_1 = H_0^{(1)} + H_{rf}$$
, (2.2.12)

and

$$H_2 = H_0^{(1)} + H_0^{(2)} . \qquad (2.2.13)$$

The density superkets (Eq. (2.1.10)) at a time t_1+t_2 becomes in the frame rotating at ω_0 (interaction representa-

and

tion),

$$\boldsymbol{\rho}^{\bullet}(t_1 + t_2) = \exp(-iL_2 \cdot t_2) \exp(-iL_1 \cdot t_1) \boldsymbol{\rho}(0) \quad , \qquad (2.2.14)$$

and

$L_1 \cdot $	=	$_{H_1}\cdot$	8	Е	-	$E\otimes{}^tH_1\cdot$, and the lives bas	(2.2.15)
L2 ·	=	H2 *	\otimes	Е	-	$E \otimes {}^t H_2 \cdot $,	(2.2.16)

where

H1 •	=	Ho .	+	Hrf*,	(2.2.17)
H2 •	=	He *	,		(2.2.18)

and

H₽.	=	H _Q ' =	H _Q (1)	+	H0(5)	,	(2.2.19)
Hr f		$= \omega_1 I_X$					(2.2.20)

In Eq. (2.2.14) $\rho(0)$ is the density superkets at thermal equilibrium. In the high temperature approximation, it yields

$$\boldsymbol{\rho}(0) = (1 - \hbar\omega_e I_z/kT)/(2I+1) , \qquad (2.2.21)$$

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

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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

$$H_{1} = \begin{pmatrix} 0 & \sqrt{3}\omega_{1}/2 & 0 & 0 \\ \sqrt{3}\omega_{1}/2 & 0 & \omega_{1} & 0 \\ 0 & \omega_{1} & 0 & \sqrt{3}\omega_{1}/2 \\ 0 & 0 & \sqrt{3}\omega_{1}/2 & 0 \end{pmatrix} .$$
(2.2.22)

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

$$R = \left(\begin{array}{cccc} \sqrt{3} & 1 & -1 & \sqrt{3} \\ -1 & \sqrt{3} & \sqrt{3} & 1 \\ -1 & \sqrt{3} & -\sqrt{3} & -1 \\ \sqrt{3} & 1 & 1 & -\sqrt{3} \end{array}\right) / 2\sqrt{2} , \qquad (2.2.23)$$

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 ω_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

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 $H' = \left(\begin{array}{cc} 0 & \omega_1 \\ \omega_1 & 0 \end{array}\right)$

(2.2.24)

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 $(I+1/2)\omega_1$ [2].

In summary, when quadrupole interaction is weak enough compared with the strength of the rf field, then the magnetization nutates at ω_1 , and in the opposite case the magnetization nutates at $(I+1/2)\omega_1$.

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

H1	=	ωe	$\sqrt{3\omega_1/2}$	0	0]	
		√3ω ₁ /2	-ω0	ω1	0		
		0	ω1	-ωa	√3w1 /2		
		lo	0	$\sqrt{3\omega_1/2}$	ωg],	(2.2.25)

where ω_0 is defined in Eq. (2.2.9). This Hamiltonian can be diagonalized through the similarity transformation by the orthogonal matrix [6]

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$$Q = \begin{pmatrix} \cos\theta_{-} & -\sin\theta_{-} & -\sin\theta_{+} & \cos\theta_{+} \\ \sin\theta_{-} & \cos\theta_{-} & \cos\theta_{+} & \sin\theta_{+} \\ \sin\theta_{-} & \cos\theta_{-} & -\cos\theta_{+} & -\sin\theta_{+} \\ \cos\theta_{-} & -\sin\theta_{-} & \sin\theta_{+} & -\cos\theta_{+} \end{pmatrix} / \sqrt{2} ,$$

$$(2.2.26a)$$

$$\tan 2\theta_{\pm} = (\sqrt{3}/2)\omega_{1}/(\omega_{0} \pm \omega_{1}/2) ,$$

$$(2.2.26b)$$

and the corresponding eigenvalues are

 $\lambda_{1} = \omega_{1}/2 + (\omega_{1}^{2} + \omega_{0}^{2} - \omega_{1} \omega_{0})^{1/2} ,$ $\lambda_{2} = \omega_{1}/2 - (\omega_{1}^{2} + \omega_{0}^{2} - \omega_{1} \omega_{0})^{1/2} ,$ $\lambda_{3} = -\omega_{1}/2 - (\omega_{1}^{2} + \omega_{0}^{2} + \omega_{1} \omega_{0})^{1/2} ,$ $\lambda_{4} = -\omega_{1}/2 + (\omega_{1}^{2} + \omega_{0}^{2} + \omega_{1} \omega_{0})^{1/2} . \qquad (2.2.27)$

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

$$p^{*}(t_{1}) = \operatorname{Rexp}(-iL^{d}_{1}t_{1})R^{-1}p(0)$$
, (2.2.28a)

or

 $\boldsymbol{\rho}^{*}_{j}(t_{1}) = \Sigma \left[R_{jk} R_{k} | \boldsymbol{\rho}_{1}(0) \right] \exp(-i\lambda_{1} t_{1}) , \qquad (2.2.28b)$

where λ_1 is the 1-th eigenvalue of the Liouvillian. In the above Eq. (2.2.28b), $A_{j,1} = \Sigma [R_{j,k} R_{k,1} \rho_1(0)]$ is called the 'transition amplitude' which represents the intensity of the component with the frequency λ_1 .

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

$$\boldsymbol{\rho}^{\bullet}(t_1 + t_2) = \exp(-iL_2 t_2) \boldsymbol{\rho}^{\bullet}(t_1) . \qquad (2.2.29)$$

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_{\emptyset} is proportional to

```
S(t_1+t_2) \infty
```

$$\begin{split} & \{ [3\sin 2\theta - \sin 2\theta + -(1 - \cos 2\theta -)(1 + \cos 2\theta +)]\sin(\lambda_3 - \lambda_1)t_1 \\ & -[3\sin 2\theta - \sin 2\theta + +(1 - \cos 2\theta -)(1 - \cos 2\theta +)]\sin(\lambda_4 - \lambda_1)t_1 \\ & -[3\sin 2\theta - \sin 2\theta + +(1 + \cos 2\theta -)(1 + \cos 2\theta +)]\sin(\lambda_3 - \lambda_2)t_1 \\ & +[3\sin 2\theta - \sin 2\theta + -(1 + \cos 2\theta -)(1 - \cos 2\theta +)]\sin(\lambda_4 - \lambda_2)t_1 \} \\ & \times \exp(-i\omega_{\theta}^{(2)}t_2) , \end{split}$$

(2.2.30)

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

 $\omega_{\theta}^{(2)} = (e^{2}qQ/h)^{2}/192\omega_{\theta} \\ \times \{9(1-\cos^{2}\theta)^{2}-6\eta(1-\cos^{4}\theta)\cos 2\phi \\ +\eta^{2}(1+\cos^{2}\theta)^{2}\cos^{2}2\phi+4\eta^{2}\cos^{2}\theta(1-\cos^{2}2\phi) \\ -72(1-\cos^{2}\theta)\cos^{2}\theta-48\eta(1-\cos^{2}\theta)\cos^{2}\theta\cos 2\phi \\ -8\eta^{2}(1-\cos^{2}\theta)\cos^{2}\theta\cos^{2}2\phi \\ -8\eta^{2}(1-\cos^{2}\theta)(1-\cos^{2}2\phi)\} .$ (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.

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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.,

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

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

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

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

$$k_{j1} + k_{j2} + \ldots + k_{jm} = 0$$
 (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.

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In principle, in the case where the chemical exchangae occurs among the m sites, the density superkets ρ is defined by [8]

$$\boldsymbol{\rho} = \boldsymbol{\rho}^{(1)} \otimes \boldsymbol{\rho}^{(2)} \otimes \dots \otimes \boldsymbol{\rho}^{(m)} , \qquad (2.3.4)$$

where $\rho^{(j)}$ represents the density superkets at the j-th site and × 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 :

$$\boldsymbol{\rho} = \boldsymbol{\rho}^{(1)} \oplus \boldsymbol{\rho}^{(2)} \oplus \dots \oplus \boldsymbol{\rho}^{(m)} , \qquad (2.3.5)$$

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

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

where L^(j) is the Liouvillian corresponding to the j-th

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site.

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

$$dp/dt = -(iL+K)p$$
, (2.3.7)

and

K =	K1 1	K1 2	K1 3	 k1 m		
	K2 1	K2 2	K2 3	 k 2 m		
			•		⊗ Ек ,	
	km 1	Km 2	Кт з	 km m	J	(2.3.8)

where EK is (2I+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\)} =$	=	La (j)	+	Lc s (j)	,		(2.4.1a)
L(1)2	=	Le (j)	+	Lcs(j)	+	Lrr .	(2.4.1b)

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

$$K = \begin{pmatrix} k_1 & -k_2 \\ -k_1 & k_2 \end{pmatrix} \otimes E_K \quad . \tag{2.4.2}$$

Thus the density superkets at a time t1+t2 becomes

$$\rho(t_1+t_2) = \exp\{-(iL_2+K)t_2\}\exp\{-(iL_1+K)t_1\}\rho(0),$$
(2.4.3)

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. i) Slow motion regime : k_1 , k_2 << H_{θ} , H_{rf}

In this case the chemical exchange effect can be treated as a perturbation because the effect on the spectrum from

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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):

$$L^{d} = \begin{pmatrix} Q^{-1} \begin{pmatrix} (1) & 0 \\ 0 & Q^{-1} \begin{pmatrix} (2) \end{pmatrix} \end{pmatrix} \begin{pmatrix} L^{(1)} & 0 \\ 0 & L^{(2)} \end{pmatrix} \begin{pmatrix} Q^{(1)} & 0 \\ 0 & Q^{(2)} \end{pmatrix}$$
$$= \begin{pmatrix} L^{d} \begin{pmatrix} (1) & 0 \\ 0 & L^{d} \begin{pmatrix} (2) \end{pmatrix} \end{pmatrix}.$$
(2.4.4)

And the exchange matrix becomes

$$\mathbf{K}^{s} = \begin{pmatrix} k_{1} E_{K} & -\mathbf{Q}^{(1)-1} k_{2} \mathbf{Q}^{(2)} \\ -\mathbf{Q}^{(2)-1} k_{1} \mathbf{Q}^{(1)} & k_{2} E_{K} \end{pmatrix} .$$
(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 δ_{ij} stands for the Kronecker's delta. The Liouvillian is not altered and the exchange matrix becomes

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$$\begin{split} \mathbf{K}^{\mathrm{S}} &= \begin{pmatrix} 1/\sqrt{\mathbf{p}_{1}} & \mathbf{0} \\ \mathbf{0} & 1/\sqrt{\mathbf{p}_{2}} \end{pmatrix} \begin{pmatrix} -\mathbf{k}_{1} & \mathbf{k}_{2} \\ \mathbf{k}_{1} & -\mathbf{k}_{2} \end{pmatrix} \begin{pmatrix} \sqrt{\mathbf{p}_{1}} & \mathbf{0} \\ \mathbf{0} & \sqrt{\mathbf{p}_{2}} \end{pmatrix} \otimes \mathbf{E}_{\mathrm{K}} , \\ &= \begin{pmatrix} -\mathbf{k}_{1} & \mathbf{k}^{*} \\ \mathbf{k}^{*} & -\mathbf{k}_{2} \end{pmatrix} \otimes \mathbf{E}_{\mathrm{K}} . \end{split}$$

This can be diagonalized by

$$\begin{aligned} \mathbf{K}^{d} &= \begin{pmatrix} \cos \Phi & -\sin \Phi \\ \sin \Phi & \cos \Phi \end{pmatrix} \begin{pmatrix} -\mathbf{k}_{1} & \mathbf{k}' \\ \mathbf{k}' & -\mathbf{k}_{2} \end{pmatrix} \begin{pmatrix} \cos \Phi & \sin \Phi \\ -\sin \Phi & \cos \Phi \end{pmatrix} \otimes \mathbf{E}_{\mathsf{K}} , \\ &= \begin{pmatrix} -(\mathbf{k}_{1} + \mathbf{k}_{2}) & 0 \\ 0 & 0 \end{pmatrix} \otimes \mathbf{E}_{\mathsf{K}} , \qquad (2.4.8a) \\ &\tan 2\Phi &= 2\mathbf{k}'/(\mathbf{k}_{1} - \mathbf{k}_{2}) , \qquad (2.4.8b) \end{aligned}$$

and so the Liouvillian is expressed as

$$L^{f} = \begin{pmatrix} L^{(1)} + L^{(2)} & 0 \\ 0 & L^{(1)} + L^{(2)} \end{pmatrix} + (L^{(1)} - L^{(2)}) \begin{pmatrix} \cos 2\Phi & \sin 2\Phi \\ \sin 2\Phi & -\cos 2\Phi \end{pmatrix}, \quad (2.4.9)$$

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 weightaveraged Liouvillian. In the case of the two-site jump the time-averaged spectrum shows a characteristic pattern depending 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

111) 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^2Qq/h (and also with ω_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.

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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 (21+1)²×(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 ^S 1	=	(P-1	$\otimes E_K$)(L ₁ + K)(P $\otimes E_K$)	
	=	L1 +	K ^s ,	(3.1.1a)
L ^S 2	=	(P-1	\otimes E _K)(L ₂ + K)(P \otimes E _K)	
	=	L2 +	K ^s ,	(3.1.1b)

where

 $K^{s} = (P^{-1} \otimes E_{K})K(P \otimes E_{K}) , \qquad (3.1.1c)$

and P is defined by Eq. (2.4.6). Then it is proved that the matrix L^{s_1} (and also L^{s_2}) can be diagonalized by a complex orthogonal matrix. (The complex orthogonal matrix means

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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 I_2 basis to I_x basis [1]. When the rows and the columns are suitably interchanged, the Liouvillian at the j-th site L_i can be factorized so as to have a blockdiagonal structure whose blocks have the dimension $(2I+1)^2/4 = 4$.

$$L^{x}_{j} = (RT)^{-1}L_{j}(RT)$$

$$= \left(\begin{array}{cc} A_{j} & O \\ B_{j} \\ B^{*}_{j} \\ O & A^{*}_{j} \end{array}\right), \qquad (3.1.2)$$

and density superket at the site j becomes

$$\boldsymbol{\rho}^{X_{j}} = (RT)^{-1} \boldsymbol{\rho}_{j} , \qquad (3.1.3)$$

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

* 'I₂ basis' means that the axis parallel to the static external magnetic field is the quantization axis. Thus I_2 becomes good quantum number. Also, 'I_x basis' means that the axis parallel to the rf field is the quantization axis and in this choice of the basis, I_x is good quantum number.

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orthogonal matrix which operates to transform the basis from I_Z to I_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 :

$$\begin{split} A_{j} &= \left(\begin{array}{ccccc} 0 & \sqrt{3}\omega_{0,j} & -\sqrt{3}\omega_{0,j} & 0 \\ \sqrt{3}\omega_{0,j} & -2\omega_{0,j} + 4\omega_{1} & 0 & -\sqrt{3}\omega_{0,j} \\ -\sqrt{3}\omega_{0,j} & 0 & 2\omega_{0,j} - 4\omega_{1} & \sqrt{3}\omega_{0,j} \\ 0 & -\sqrt{3}\omega_{0,j} & \sqrt{3}\omega_{0,j} & 0 \\ \end{array} \right) \\ (3.1.4a) \\ B_{j} &= \left(\begin{array}{ccccc} 2\omega_{0,j} + 2\omega_{1} & \sqrt{3}\omega_{0,j} & \sqrt{3}\omega_{0,j} & 0 \\ \sqrt{3}\omega_{0,j} & 6\omega_{1} & 0 & \sqrt{3}\omega_{0,j} \\ \sqrt{3}\omega_{0,j} & 6\omega_{1} & 0 & \sqrt{3}\omega_{0,j} \\ \sqrt{3}\omega_{0,j} & 0 & -2\omega_{1} & \sqrt{3}\omega_{0,j} \\ 0 & \sqrt{3}\omega_{0,j} & \sqrt{3}\omega_{0,j} & -2\omega_{0,j} + 2\omega_{1} \\ \end{array} \right) \\ B^{*}{}_{j} &= \left(\begin{array}{ccccc} -2\omega_{0,j} - 2\omega_{1} & -\sqrt{3}\omega_{0,j} & 0 \\ -\sqrt{3}\omega_{0,j} & -6\omega_{1} & 0 & -\sqrt{3}\omega_{0,j} \\ \sqrt{3}\omega_{0,j} & 0 & -2\omega_{1} & -\sqrt{3}\omega_{0,j} \\ \sqrt{3}\omega_{0,j} & 0 & -2\omega_{1} & -\sqrt{3}\omega_{0,j} \\ \sqrt{3}\omega_{0,j} & 0 & -2\omega_{1} & -\sqrt{3}\omega_{0,j} \\ \sqrt{3}\omega_{0,j} & 0 & -2\omega_{0,j} - 2\omega_{0,j} - 2\omega_{0,j} \\ \end{array} \right) \\ A^{*}{}_{j} &= \left(\begin{array}{ccccc} 0 & -\sqrt{3}\omega_{0,j} & \sqrt{3}\omega_{0,j} & 0 \\ -\sqrt{3}\omega_{0,j} & 2\omega_{0,j} + 4\omega_{1} & 0 & \sqrt{3}\omega_{0,j} \\ \sqrt{3}\omega_{0,j} & 0 & -2\omega_{0,j} - 4\omega_{1} & -\sqrt{3}\omega_{0,j} \\ \sqrt{3}\omega_{0,j} & 0 & -2\omega_{0,j} - 4\omega_{1} & -\sqrt{3}\omega_{0,j} \\ \sqrt{3}\omega_{0,j} & 0 & -2\omega_{0,j} - 4\omega_{1} & -\sqrt{3}\omega_{0,j} \\ \sqrt{3}\omega_{0,j} & 0 & -2\omega_{0,j} - 4\omega_{1} & -\sqrt{3}\omega_{0,j} \\ \sqrt{3}\omega_{0,j} & 0 & -2\omega_{0,j} - 4\omega_{1} & -\sqrt{3}\omega_{0,j} \\ \end{array} \right) \\ \end{array} \right) \\ (3.1.4c) \end{split}$$

where $\omega_{0,j}$ represents the first order quadrupole interaction at the site j. The corresponding density superkets at j-th

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site transformed as the Liouvillian are given by :

 $\boldsymbol{\rho}^{\chi}_{i} = p_{i}^{t} (\ 0 \ 0 \ 0 \ 0 \ \sqrt{3} \ 3 \ 0 \ -\sqrt{3} \ \sqrt{3} \ 3 \ 0 \ -\sqrt{3} \ 0 \ 0 \ 0 \ 0 \) \,.$ (3.1.5)

Because the elements of the density superkets corresponding to the matrices A and A' on the basis I_X 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

$$L^{S}_{1} = \begin{pmatrix} iB_{1} - k_{1}E_{B} & k'E_{B} \\ k'E_{B} & iB_{2} - k_{2}E_{B} \end{pmatrix}, \qquad (3.1.6)$$

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

Although the I_x 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 I_Z . Then it has to be put back to the I_Z 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, $L^{s}{}_{2}$ ', 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

 $S(t_{2}, t_{1}) \propto I_{X} \rho(t_{2}, t_{1})$ = $\Sigma P_{i} : Q_{2} : j \exp[-iL_{2}d_{j}t_{2}]Q_{2}^{-1} : j_{k}$ × $R_{k} : Q_{1} : m \exp[-iL_{1}d_{m}t_{1}]Q_{1}^{-1} : m n \rho_{X}(0)_{n}$, (3.1.7)

where Q_1 and Q_2 are complex orthogonal matrices which diagonalize L^{s}_1 ' and L^{s}_2 ', respectively.

The Liouvillians L^{s}_{1} and L^{s}_{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

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	 •	•	•	•		
and the second second	 •	•		•		
$J(j,j,\chi) =$	 1	0	0	0		
	 0	COSX	sinχ	0	 i)	
012 07 158	 0	-sin x	cosx	0	 j)	
	 0	0	0	1		
C. C	 •					
and industry and			•	•].	

(3.1.8)

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

 $L^{T} = \Pi(J^{-1})L^{S}\Pi J_{1} , \qquad (3.1.9)$

where L^{T} 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_{j} is suitably selected so as to realize the factorization $A_{j}-s_{j}E=Q_{j}R_{j}$ where Q_{j} is a complex orthogonal matrix and R_{j} is an upper triangular matrix, then $A_{j+1} = Q_{j}^{-1}A_{j}Q_{j}$ 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

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triangular matrix. Since A_{0} 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 2×2 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,...r, rotation angle is determined such that the element (r+1,i) 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]:

$$f(t_2, t_1) = \int d\phi \int \sin\theta d\theta \ S(t_2, t_1)$$
 (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 :

Rc =	cosθcosφ	cosθsinφ	-sinθ		
	-sinφ	cosφ	0		
	sinecosø	sinθsinφ	cosθ].	(3.1.11)

where θ and ϕ 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 α , β , and γ in the crystalline frame by :

$$R_{j} = \begin{pmatrix} \cos\alpha \sin\alpha & 0 \\ -\sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \cos\beta & 0 & -\sin\beta \\ 0 & 1 & 0 \\ \sin\beta & 0 & \cos\beta \end{pmatrix} \begin{pmatrix} \cos\gamma & \sin\gamma & 0 \\ -\sin\gamma & \cos\gamma & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

$$(3.1.12)$$

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

$$R_{j}'(\theta_{j}, \phi_{j}) = R_{j}R_{c}$$
 (3.1.13)

Here, the terms needed in the actual calculation are

 $Z_j^2 = \cos^2 \theta_j$, $x_j^2 - y_j^2 = \sin^2 \theta_j \cos 2 \phi_j$, (3.1.14)

where

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 $x_{c} = sin\theta cos\phi$, $y_c = sin\theta cos\phi$, $Z_c = \cos\theta , \qquad (3.1.16)$

where θ_j and ϕ_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

$$\omega_{Q}^{(1)}_{j} = e^{2}qQ/8I(2I-1)\{3z_{j}^{2}-1+\eta(x_{j}^{2}-y_{j}^{2})\}, (3.1.17)$$

$$\omega_{Q}^{(2)}_{j} = (e^{2}qQ/h)^{2}/192\omega_{R}$$

$$\{9(1-z_{j}^{2})^{2}-6\eta(1+z_{j}^{2})(x_{j}^{2}-y_{j}^{2})$$

$$+4\eta^{2}z_{j}^{2}+\eta^{2}(x_{j}^{2}-y_{j}^{2})^{2}$$

$$-72z_{j}^{2}(1-z_{j}^{2})-48\eta z_{j}^{2}(x_{j}^{2}-y_{j}^{2})^{2}$$

$$-8\eta^{2}(1-z_{j}^{2})+8\eta^{2}(x_{j}^{2}-y_{j}^{2})^{2}\}.$$

$$(3.1.18)$$

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

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

$$f(t_2, t_1) = \int d\phi \int d(\cos\theta) S(t_2, t_1)$$
. (3.1.19)

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

In the case where only one kind of site exists, one can tentatively coincide the crystalline frame with the EFG

and

principal axes. Since $S(t_2,t_1)$ is symmetric with respect to $\cos\theta$ and ϕ , 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).

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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 I \geq 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 θ and ϕ 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 $0 \le \cos\theta < 1$, and $0 \le \phi < \pi$.

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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^2qQ/h , η 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 θ and ϕ 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 $-\pi < \phi \le \pi$.

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 128×256 are used to calculate the FID's. The program lists are given in

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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.

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4. Sample

4.1. NaNO2 and NaHgCl3.2H2O

NaNO₂ crystallizes in an orthorhombic (space group lm2m) crystal system with the unit cell dimension of a = 3.569 Å, b = 5.563 Å, and c = 5.384 Å, Z = 2. [1]

Crystal of NaHgCl₃.2H₂O is orthorhombic (space group Pnma) with four molecules in the unit cell [2]. The lattice parameters are : a = 9.372 Å, b = 4.037 Å, and c = 18.71 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 Na2 SeO3

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. Na1+x Zr2 Six P3-x 012

The system $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ 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 ($0.0 \le x \le 1.8$, $2.2 \le x \le 3.0$) and C2/c ($1.8 \le x \le 2.2$). The latter is a slightly deformed structure of the former. The structure consists of a threedimensional skeletal network of PO₄ (and/or SiO₄) tetrahedra which are corner-shared with ZrO_6 octahedra. The ZrO_6 octahedron is linked by three PO₄ tetrahedra so as to form a ribbon along the hexagonal c-axis and also linked by six PO₄









Crystal structure of $Na_{1+x} Zr_2 Si_x P_{3-x} O_{12}$.

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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 (NaZr₂P₃O₁₂), sodium occupies the site 1 (Na⁽¹⁾) only which is an octahedral site surrounded by six oxygen atoms of ZrO₆, 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 O²⁻. Thus it has been supposed that the sodium ion transport occurs through the path Na⁽¹⁾ \rightarrow Na⁽²⁾ \rightarrow 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} Zr₂Si_x P_{3-x}O₁₂ brings about information on the dynamic process and the microscopic mechanism of the ion conduction in this material.

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5. Experiment

5.1. Sample Preparation

5.1.1. NaNO₂ and NaHgCl₂.2H₂O

 $NaNO_2$ is of commercial source (Nacalai Tesque, guaranteed reagent grade, purity 98.0%) and used without further purification.

NaHgCl₃.2H₂O was prepared from aqueous solution of the appropriate mixture of NaCl (Tomita Seiyaku) and HgCl₂ (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 NaHgCl₃.2H₂O but indicated at once the existence of small amount of HgCl₂. However, this HgCl₂ impurity is supposed to have little influence on the NMR of 23 Na.

5.1.2. Na2 SeO3

 Na_2SeO_3 was prepared from aqueous solution of a stoichiometric mixture of NaOH (Nacalai Tesque, reagent grade, purity 93%) and selenius acid H_2SeO_3 . [2] H_2SeO_3 is prepared by dissolving SeO_2 (Nacalai Tesque, guaranteed reagent grade, purity 98%) in water. Slow evaporation of the solution gave the white powder.

5.1.3. Na1+x Zr2 Six P3-x O12

The powdered specimen was synthesized from the stoichiometric mixture of Na_2CO_3 : ZrO_2 : SiO_2 : $NH_4H_2PO_4$ = 1+x : 4 : 2x : 2(3-x), x=0.0, 1.0, and 2.0. [2] The reagents used here were : Na_2CO_3 , Nacalai Tesque, guaranteed reagent grade, purity 99.5%; ZrO_2 , Nacalai Tesque, reagent grade;

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SiO₂, Nacalai Tesque, guaranteed reagent grade; $NH_4H_2PO_4$, Wako Junyaku, guaranteed reagent grade, purity 98%. The mixture was at first heated to 900 °C for several hours to decompose Na_2CO_3 and $NH_4H_2PO_4$, 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.





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SAMPLE NAME: Na32r2Si2P TARCET : Cu VOL and CUR: 40KV 40mA SLITS : DS 1 RS .3 SS 1 SCAN SPEED: 3 DEG/MIN. STEP/SAMPL.: .02 DEG PRESET TIME: 0 SEC FILE NAME :03100 OPERATOR : YAMAMOTO COMMENT :

DATE:89.10.27

SMOOTHING NO.: 11 THRESH.INTEN.: 137 CPS 2nd DERIV.: 263 CPS/(DEGxDEG) WIDTH: .09 DEG B.G.REDUCTION:NO EXECUTION OUTPUT FILE :

Sample Name : Na3Zr2S12P





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5.2 Nutation NMR

The ²³Na 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 ~±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 µs every 1 µs, or from 2 to 256 µs every 2 µs by the use of the automation program. The FID signal was sampled every 0.8 μ s. The number of data points was usually 1k words. Each FID was guadrature-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 ±1 K.

In order to minimize the effect of the rf pulse inhomogeneity, the samples were sealed in the glass ampules with $10 \text{mm}\phi$ in ca. 10 mm 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

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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].

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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 F₂ 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, F₁, 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, H₂, does not contain any useful information other than quadrupole interaction, an FT over t₁ gives nutation spectrum which gives rise directly to the ratio $\Omega_Q/\omega_1 = [3e^2Qq/2I(2I-1)\hbar]/\omega_1$, where Ω_Q 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 ω_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 ω_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 ω_1 in the case of $e^2Qq/h = 0$, indicating that



Figure 6.1

Stacked plot of 2D nutation spectrum simulated with parameters $e^2Qq/h = 0.2$ 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 F_1 and b) F_2 axis, respectively.

only the transition between $m = \pm 1/2$ can be excited by weak rf field.

The variation of the nutation spectrum with η 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 η . 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

 $\sqrt{A(\omega)^2 + D(\omega)^2}$,

where A and D are absorption (real) and dispersion (imaginary) components of the spectrum.



Dependence of nutation spectrum on the strength of quadrupole interaction.





6.2 Data Analysis

1) NaNO₂ and NaHgCl₃.2H₂O

The 2D nutation spectrum of NaNO₂ is shown in Fig. 6.5, and its projection onto the F₁ axis is shown in Fig. 6.6a. Three broad peaks are found at near 0, ω_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 $e^2Qq/h \simeq 1.1$ MHz which has been reported in the literature [1]. The projection onto the F₂ axis (Fig. 6.6b) gives the structure due to the second order quadrupole interaction, and η can be estimated from its line shape to be $\simeq 0.1$.

The spectrum of NaHgCl₃.2H₂O is shown in Fig. 6.7, which resembles with that of NaNO₂, but the relative intensities of the peaks are different (See Fig. 6.8.). This spectrum corresponds to the spectrum of $e^2Qq/h \simeq 0.6$ MHz and $\eta \simeq 0.2$. 3) 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 ω_1 and that near ω_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 η is estimated to be 0.8 and 0.0 for a and b. No significant temperature

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Figure 6.5

Contour plot of 2D nutation spectrum of $\ensuremath{\mathsf{NaNO}}_2$ at room temperature.

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2D nutation spectrum of $NaNO_2$ at room temperature. a) Projection onto F₁ axis. b) Projection onto F₂ axis.

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Figure 6.7

Contour plot of 2D nutation spectrum of NaHgCl₃.2H₂O at room temperature.

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Figure 6.8

2D nutation spectrum of NaHgCl_3.2H_2O. Projection onto F_1 axis.

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Contour plot of 2D nutation spectrum of $\mathrm{Na}_2\,\mathrm{SeO}_3$ at room temperature.

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dependence was found except at the highest temperature (330 K), at which a sharp peak appeared at ω_1 . This peak corresponds obviously to very small quadrupole interaction but the origin of such small e^2Qq/h is not clear. 4) Na_{1+x} Zr₂Si_{3-x} P_xO₁₂

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 F₂ axis (except the spectral component

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Contour plot of 2D nutation spectrum of $NaZr_2Si_3O_{1\,2}$ at room temperature.





Contour plot of 2D nutation spectrum of $Na_3 Zr_2 SiP_2 O_{1\,2}$ at 116 K.



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Figure 6.14

Contour plot of 2D nutation spectrum of Na₃Zr₂SiP₂O₁₂ at 186 K.



Figure 6.15

Contour plot of 2D nutation spectrum of $Na_3Zr_2SiP_2O_{1\,2}$ at 237 K.



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Figure 6.16

Contour plot of 2D nutation spectrum of $Na_3 Zr_2 SiP_2 O_{1\,2}$ at 300 K.



Contour plot of 2D nutation spectrum of $Na_3 Zr_2 SiP_2 O_{1\,2}$ at 363 K.



Appeared at around 5 frequency is the 5, dimension is shown in 55, 575. Using the store values of store the states the of the best littley to the providential line disks was obtained by mutating y = 10 between 1) and 5.2 little 2. and that difference between the countral shorts at the loss slive is in the theorematic are manyeried by the crystal take to be size i had three Hild sympletry and so a should be 0. In the theorematic contains and it discovers between the bits slive best broken the contains of the discoverse between the bits slive between this correspondent to well define one size over at the bighter interaction is well and the discoverse size over at the bighter interaction by the the rapid charter of size over at the bighter interaction by the first 5.4% and 32.



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Figure 6.19

Projection onto F_2 axis of 2D nutation spectrum of $Na_3Zr_2SiP_2O_{12}$ at 116K.

values apparent always on this coincide with

appeared at around 0 frequency in the F₁ 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 η 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 $e^2Qg/h = 1.1$ 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 $E_a \simeq 13$ kJ/mol. On the other hand the activation energy values obtained above do not coincide with that found in the conductivity measurement ($E_a \simeq 31 \text{ kJ/mol}$) [2]. The large

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Projection onto F_1 axis of 2D nutation spectrum of Na₃Zr₂SiP₂O₁₂ at 363K.



Contour plot of 2D nutation spectrum simulated with chemical exchange rate k = 0.001 kHz. Other parameters are described in the text.



Contour plot of 2D nutation spectrum simulated with chemical exchange rate k = 0.01 kHz.



Contour plot of 2D nutation spectrum simulated with chemical exchange rate k = 0.1 kHz.



Contour plot of 2D nutation spectrum simulated with chemical exchange rate k = 1.0 kHz.



Contour plot of 2D nutation spectrum simulated with chemical exchange rate k = 10 kHz.

discrepancy between the $E_{\mathfrak{s}}$'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.

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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 $3/2 \sim 9/2$ and to systems with and without chemical exchange.

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

1. The 23 Na resonances in NaNO₂ and NaHgCl₃.2H₂O were used to establish the optimal experimental conditions for the 2D

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nutation spectra and to evaluate the sensitivity of the spectra to the quadrupole interaction parameters, e^2Qq/h and η .

2. The ²³Na nutation NMR was applied to Na₂SeO₃ to distinguish the three crystallographically nonequivalent Na sites in this compound. The value e²Qq/h at the individual sites could be determined and also η was estimated for two of the three sites in this material.

3. The ²³Na 2D nutation NMR was used to examine the dynamic process of $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$. 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.

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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 ~ 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 ²³Na, ²⁷Al, ³⁹K, ⁵⁹Co, etc. give often e²Qq/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 $\Omega_{\rm Q}/2\pi$ 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_D , $H_{CS} \ll H_{rf}$ holds, undesirable line broadening effect due to H_D and H_{CS} 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

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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

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$$S(t) \propto [\alpha(1-\cos 2\Omega t)+i\beta \sin 2\Omega t)]$$
,

(7.2.1)

2.2)

where

$$\Omega = \sqrt{\Delta\omega^2 + \omega_1^2} ,$$

$$\alpha = \omega_1 \Delta\omega/\Omega^2 ,$$

$$\beta = \omega_1/2\Omega . \qquad (7.$$

Since $\Delta \omega \neq 0$, α 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 F₁ 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 Ω_{0}/ω_{1} and it causes the line broadening in F₁ 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 Ω_0/ω_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) t₁ 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 depends on t_1 (and the recycle time) the peaks at $2\omega_1$, $3\omega_1$, ... 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 nearestneighbor 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

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encountered. [5] In the case that the ion transport occurs through the hopping between two or more nonequivalent ionic sites as was found in Na1+x Zr2Six P3 x O12, 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 Na1+x Zr2Six P3-x O12 are considered to apply to such a model. The 2D nutation NMR mothod 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.)

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Figure 7.2

Nonequivalent site model with deep and shallow wells.

References

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 - A. Samoson and E. Lippmaa,
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Line#	Source	e Line	Mici	osoft	FORTRAN	Optimizir	g Compiler	Version 4.01
1 2 3	\$NOTRI \$DECL	JNCATE ARE PROGRAM NUT/	NT I ON					
4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 9 20	C	COMPLEX*16 / COMPLEX*16 I REAL*8 7 REAL*8 / INTEGER*4 I CHARACTER*1	ARYDAT(1, E1(10),EI CHD(10),C A1,W0,P12 DIM(2),MX 5 RGF,TDI	1024), E(10),F QCC,ETA 2,T1(2) (D(2),N	H1(100) REC(10), A,QC2,W1 ,CT1,CT ISP,NT,N	R1(100),R ERC(10),W(Q1F(10),W 2(20000),C MXT,I,J,	DR(100) 10) 1F(10) P1(900),H1 K,L,N,ERS	I(2,100),S,D
	C	EQUIVALENCE COMMON /ARYI COMMON /PARA COMMON /WRK	(H1,H1I) DAT/ARYD/ MS/THD,G /AR/RDR,H	,(CT2) AT,DIM ACC,ETA EE,REC,	901),CP ,QC2,Q11 ERC,W	1(1)) 7,W1F		
	C	Declaratio	ons of Co	onstant	s			
	С	PARAMETER(P DATA MXD/102	12=6.283	853071	79586D+	00)		
21	C	Spin Numbe	er					
23 24 25 26 27	С	WRITE(*,'(A READ(*,'(I2) S=DBLE(NSP)) AI=S*S+S	(1¥)') '()') NSP /2.0D+00)Spin ≯	£2 = '			
28 29 30 31 32	C C	Lamor Free	mency					
	C	WRITE(*,'(A) READ (*,'(F)	20¥)') '('.4)') W(Lamor	Freq / I	MHz = '		
33 34	C	Quadrupole	e Interac	tion F	arameter	°S		
35 36 37	C	WRITE(*,'(A) READ (*,'(2)	(7¥)') '(10.6)')	eqQ / QCC,ET	MHz, η Λ	= '		
39	C	RF Strengt	h in Fre	quency	Units			
40 41 42 43 44 45 46 47 48 49 50 51 52 53	C	WRITE(*,'(A2 READ (*,'(F0	27¥)') '(5.3)') W1	RF Fie	ld Stre	ngth / kHz	= '	
	CCC	Sampling I	Points in	each	Dimensio	on		
	300	DO 300 I=1,2 WRITE(*,'(WRITE(*,'(* 'Number READ (*,'(WRITE(*,'(READ (*,'(CONTINUE	2 A13,I1)' A35,I4,A of Samp (15)') D1 A25¥)') (F5.3)')) 'ODi (5¥)') ling P M(I) ' Tim TI(I)	mension Voints (Ne Increm	: ', I Max. ',MX nent / μs	D(I),') =	

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Line#	Sourc	e Line Microsoft FORTRAN Optimizing Compiler Version 4.01					
54 55 56	C C C	RGF : Stores Computational Condition TDF : Saves FID Data					
57 58 59 60 61	C	<pre>WRITE(*,'(A25¥)') 'ORegistry File Name = ' READ(*,'(A15)') RGF WRITE(*,'(A25¥)') ' Time Domain File Name = ' READ(*,'(A15)') TDF</pre>					
62 63 64	CCC	Get the Number to be calculated					
64 65 66 69 70 71 72 73 74 75 76 77 78 79	400	<pre>WRITE(*, '(A20)') ' Number of Division over θ ' WRITE(*, '(A¥)') ' [Max. : 20000 (η = 0) 900 (η > 0)] = ' READ(*, '(15)') NT DO 400 I=1,NT CT1=DBLE(I)/DBLE(NT) CT2(I)=CT1*CT1 CONTINUE IF (ETA .EQ. 0.0D+00) THEN NP=1 CP1(1)=0.0D+00 ELSE NP=NT DO 410 I=1,NP CP1(I)=ETA*DCOS(PI2*DBLE(I)/DBLE(NT)) CONTINUE</pre>					
81 82	C C	Store the Parameters					
83 84 85 86 87 88 90 91 92 93 94 95 96 97 98 99	C 500	OPEN (UNIT=50, FILE=RGF, ACCESS='SEQUENTIAL') WRITE(50, '(A40)') ' Computational Conditions ' WRITE(50, '(A16)') '< Interactions >' WRITE(50, '(A10,I2,A4)')' Spin = ',NSP,' / 2' WRITE(50, '(A22,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 Increments' DO 500 I=1.2 WRITE(50, '(7X,I1,10X,I4,9X,F10.5)') I,DIM(I),TI(I) CONTINUE WRITE(50, '(/A28, I5)') ' Total Division over θ = ',NT WRITE(50, '(/A18,A15)') ' Data Stored in ',TDF					
99		CLOSE (UNIT=50)					

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Line#	Source	e Line	Microsoft FORTRAN Optimizing Compiler Version 4.01		
100 101 102 103 104 105 106 107 108 109 110 111 112 113 114 115	C C	Determine the	Parameters suitable to Calculation		
	600 C	QCC=QCC/DBLE(NSP*NSP-NSP)*2.5D-01 QC2=QCC*QCC/W0*PI2*TI(2)*(AI-7.5D-01) QCC=QCC*PI2*TI(1) W1=W1*PI2*TI(1)*1.0D-03 D=DBLE(NSP)/2.0D+00 D0 600 I=1,NSP+1 THD(I)=D Q1F(I)=D*D*3.0D+00-AI W1F(I)=W1*DSQRT(AI-D*(D-1.0D+00))/2.0D+00 D=D-1.0D+00 CONTINUE WRITE(*, '(A38,I5/)') & ' Total Division over THETA, PHI = ',NT*NP			
117	C	Powder Averag	ing Start here		
110 119 120 121 122 123 124 125 126 127 128 129 130 131 132 133 134 135 136 137 138 139 140 141 142 143 144 145 146 147 148 149 150 151	700 710	DO 710 I=1,NT WRITE(*,'(A30 DO 700 J=1,NP CALL EVOLVE IF (ERS .NE CONTINUE CONTINUE	,15)') '+ Powder Averaging Now : ',I*NP (NSP+1,H1,H11,R1,E1,CT2(I),CP1(J),ERS) . 0) GOTO 20000		
	C C	Normalize and	Store the Data		
	C 800 810 9000	OPEN (UNIT=10, D=1.0D+00/DBLE() DO 810 I=1,DIM(DO 800 J=1,DIM ARYDAT(J,1) WRITE(10, FI CONTINUE CONTINUE CLOSE (UNIT=10) FORMAT(D22.16,1)	FILE=TDF) NT*NP) 1) M(2) =ARYDAT(J,I)*D MT=9000, 10STAT=ERS, ERR=10000) ARYDAT(J,I) K,D22.16)		
	C	Normal End.			
	С	GO TO 99999			
	C	Error Exist i	n the Procedure.		
	C 10000 20000 C 99999 \$PAGE	WRITE(*,'(A18,I GO TO 99999 WRITE(*,'(A23,I END	5)') ' File Write Error ',ERS 5)') ' Diagonalization Error ',ERS		
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Line#	Su	urc	e Line Microsoft FORTRAN Optimizing Compiler Version 4.01
152			SUBROUTINE EVOLVE(L, HI, HII, RI, EI, CT2, CP1, ERR)
153	C		Calculate the Evolution of the Density Vectors
155	С		
156			COMPLEX*16 ARYDAT(1,1024),H1(L,L),R1(L,L),E1(L),IC,Q2E
157			CUMPLEX*16 RDR(10,10), $EE(10)$, $REC(10)$, $ERC(10)$, $W(10)$
150			REAL $*$ 0 HII(2,L,L), \forall I, \forall 2, D, CI2, CI4, SI2, SI4, CFI, CF2, SF2 REAL $*$ 8 THD(10) ACC ETA AC2 AIE(10), \forall IE(10)
160			INTEGER*4 DIM(2), N1, N2, I, J, K, ERR
161	С		
162			COMMON /ARYDAT/ARYDAT,DIM
163			COMMON /PARAMS/THD,QCC,ETA,QC2,Q1F,W1F
164	-		COMMON /WRKVAR/RDR, EE, REC, ERC, W
165	C		Terraforestion of Constitute to Malandan Deser
165	C		Transformation of Coordinate to Molecular Frame
168	C		СТ4=СТ2*СТ2
169			ST2=1.0D+00-CT2
170			ST4=ST2*ST2
171			CP2=CP1*CP1
172	~		SP2=ETA*ETA-CP2
173	C		Einst Onlan Quadqueala Calibling
174	c		FIFSt order Quadrupole Splitting
176	~		Q1=QCC*(3.0D+00*CT2-1.0D+00+ST2*CP1)
177	С		
178	C		Second Order Quadrupole Shift for the Central Transition
180	C		Q2=QC2*(_ST4*9, 0-(1, 0-CT4)*CP1*6, 0+(CT2*4, 0+ST4)*CP2+CT2*SP2*4, 0
181	Č		& -ST2*(CT2*(9.0+CP1*6.0+CP2)+SP2)*8.0)
182			Q2E=DCMPLX(DCOS(Q2),DSIN(Q2))
183	С		
184	C		Set the Hamiltonian
185	C		DO 00 1-1 1
187			DO 20 1=1 1
188			111(J I)=0 0D+00
189		20	CONTINUE
190		on is i	$H11(2, I, I) = Q1 \times Q1F(I)$
191			IF (I .GT. 1) H1I(2, I-1, I)=W1F(I-1)
192			IF (I .LT. L) H11(2,1+1,1)=W1F(1)
193		30	CONTINUE

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Linell	S	ourc	e Line Mi	crosoft	t FORTRAN Optimizing Compiler Version 4.01
194	(
195	C		Get the Eigenval	ues and	d Eigenvectors to Calculate Exponentials
196 197 198 199 200 201 202 203	C	100	CALL CHEQRD(L,H1,E IF (ERR .NE. 0) RE DO 100 I=1,L EE(I)=CDEXP(E1(I CONTINUE DO 110 J=1,L DO 110 I=1,L	E1,R1,ER ETURN	RR)
204 205 206			DO 110 K=1,L RDR(1,J)=RDR(I,J)+R1	$I(K, I) \times THD(K) \times RI(K, J)$
207 208 209		110	CONTINUE DO 120 I=1,L REC(I)=R1(L/2,I)		
210 211 212	C	120	ERC(I)=R1(L/2+1, CONTINUE	0	
213 214	CC		Calculate FID		
215 216 217 218 219 220		200	DO 300 N1=1,DIM(1) DO 200 J=1,L REC(J)=REC(J) ERC(J)=ERC(J) CONTINUE DO 210 L=1 L	∙EE(J) €DCONJG(I	(EE(J))
221 222 223		010	W(I)=0.0D+00 DO 210 J=1,L W(I)=W(I)+RE	EC (J) * RDI	DR(J,I)
224 225 226 227 228		210	DO 220 I=1,L IC=0.0D+00 DO 220 J=1,L IC=IC+W(J)*E	ERC(J)	
229 230 231 232		220	CONTINUE DO 300 N2=1,DIM(ARYDAT(N2,N1)= IC=IC*Q2E	2) ARYDAT(1	(N2,N1)+IC
233 234 235	С	300	CONTINUE		
236 237 238	C \$F	PAGE	END		

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Line	Sourc	e Line Microsoft FORTRAN Optimizing Compiler Version 4.01
239	C	SUBROUTINE CHEQRD(N,LC,EC,VC,ERR)
241	C	Calculate the Eigenvalues and Eigenvectors of Symmetric Matrix
242 243 244 245	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
246 247 248	C	CDABSP(ZZ)=DABS(DREAL(ZZ))+DABS(DIMAG(ZZ)) DATA DEL,ITRMAX/5.0D-15,30/
249 250	C	Set the Eigenvectors to Unit Matrix
251 252 253 254 255 256 257	100 110	DO 110 1=1,N DO 100 J=1,N VC(J,I)=0.0D+00 CONTINUE VC(I,I)=1.0D+00 CONTINUE
258	C	Search for a Small Sub-diagonal Element.
260 261 262 263 264 265 265 266 267 268	C 300 310 320	LU=N ITR=0 LL=LU IF (CDABSP(LC(LL,LL-1)) .GT. DEL) THEN LL=LL-1 IF (LL .GT. 1) GO TO 320 END IF IF (LL .NE. LU) THEN
269 270 271	CCC	If Convergence is not Attained within 30 Iterations, Truncate the Computation.
272 273	С	IF (ITR .GT. ITRMAX) GO TO 10000
274 275 276	CCCC	Determine the Origin Shift as the Eigenvalue of the 2 by 2 Bottom Submatrix which is Nearer to the bottom Element.
278 279 280 281 282 283	C	ZX=(LC(LU-1,LU-1)+LC(LU,LU))*0.5D+00 ZY=ZX-LC(LU,LU) ZZ=CDSQRT(LC(LU-1,LU)*LC(LU,LU-1)+ZY*ZY) ZZ=DSIGN(1.0D+00,CDABSP(ZY-ZZ)-CDABSP(ZY+ZZ))*ZZ+ZX LC(LL,LL)=LC(LL,LL)-ZZ ZC=1.0D+00

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Line# Source Line

Microsoft FORTRAN Optimizing Compiler Version 4.01

284 285	CCC		Left- and Right-hand Transformation.
280 287 288 289 290 291 292 293	0		DO 360 I=LL,LU-1 IP1=I+1 ZX=LC(I ,I) ZY=LC(IP1,I) ZR=CDSQRT(ZX*ZX+ZY*ZY) IF (CDABSP(ZR) .LT. DEL) GOTO 20000 LC(I,I)=ZC*ZR
294 295 296 297 298 299			IF (I .GT. LL) LC(I,I-1)=ZS*ZR LC(IP1,IP1)=LC(IP1,IP1)-ZZ ZC=ZX/ZR ZS=ZY/ZR D0 330 J=IP1,N ZY=LC(I,J)
301 302 303 304		330	LC(1P1,J)=ZY*ZC+LC(1P1,J)*ZS LC(1P1,J)=LC(1P1,J)*ZC-ZY*ZS CONTINUE DO 340 J=1,1
304 305 306 307		340	LC(J, I) =ZY*ZC+LC(J, IP1)*ZS LC(J, IP1)=LC(J, IP1)*ZC-ZY*ZS CONTINUE
308 309 310 311 312			LC(1,1)=LC(1,1)+ZZ DO 350 J=1,N ZY=VC(J,1) VC(J,1)=ZY*ZC+VC(J,1P1)*ZS VC(J,1P1)=VC(J,1P1)*ZS
312 313 314 315 316 317 318 319 320		350 360	CONTINUE CONTINUE LC(LU,LU-1)=LC(LU,LU)*ZS LC(LU,LU)=LC(LU,LU)*ZC+ZZ ITR=ITR+1 GO TO 310 END IF LU=LU-1
321 322 323	СС		IF (LU.GT. 1) GO TO 300
324 325 326	CCCC		Eigenvalues are Given by the Diagonal Elements of the Resultant Matrix.
327 328 329	U	400	DO 400 I=1,N EC(I)=LC(I,I) CONTINUE

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Line# Source Line

Microsoft FORTRAN Optimizing Compiler Version 4.01

330	С	
331	C	Normal Exit.
332	С	
333		ERR=0
334		RETURN
335	C	
336	С	Error Exit.
337	С	10000 : Not Converged.
338	С	20000 : Devide by Zero.
339	С	
340	10000	ERR=10000
341		RETURN
342	20000	ERR=20000
343		RETURN
344		END

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Source	e Line Microsoft FORTRAN Optimizing Compiler Version 4.0
\$DECLA	RE PROGRAM EXCHANGE
C	Simulation Program for 2D Nutation NMR with Chemical Exchange
C	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,PI1,PI2,SQ3 INTEGER*4 DIM(2),MXD(2),NSP,NSI,MXS,NN,MXT,I,J,N,ERS CHARACTER CHA CHARACTER*15 RGF,TDF
C	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
C	Declarations of Constants
C	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/
C	Lamor Frequency
C	WRITE(*, '(A20¥)') 'OLamor Freq / MHz = ' READ (*, '(F7,4)') W0
C C	Number of Sites to be Considered
C 1	WRITE(*,'(A18¥)') 'ONumber of Site = ' READ (*,'(I1)') NSI IF (NSI .GT. MXS) GOTO 1
00	Quadrupole Interaction Parameters and Chemical Shifts
	<pre>DO 100 I=1,NSI WRITE(*,'(A7,I1)') ' Site : ',I WRITE(*,'(A21¥)') ' eqQ / MHz, eta = ' READ (*,'(2F10.6)') QCC(1),ETA(I) WRITE(*,'(A37¥)') ' Eular Angles of Principal Axis = ' READ(*,'(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 = '</pre>

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Line# Source Line Microsoft FORTRAN Optimizing Compiler Version 4.01 59 100 CONTINUE C 60 61 C Chemical Exchange C 62 -----WRITE(*, '(AGO¥)') 63 & 'OEquilibrium Population of Each Site are Equal (Y or N) ? ' 64 READ (*, '(A1)') CHA 65 IF ((ICHAR(CHA) .EQ. ICHAR('Y')) .OR. 66 (ICHAR(CHA) .EQ. ICHAR('y'))) THEN 67 8 68 D=DBLE(NSI) DO 200 I=1,NSI 69 70 P(I)=1.0D+00/D 200 71 CONTINUE 72 ELSE 73 D=0.0D+00 74 DO 210 I=1,NSI 75 76 & 77 READ (*, '(F6.4)') P(1) D=D+P(I)78 79 210 CONTINUE DO 220 I=1,NSI 80 P(I) = P(I) / D81 82 220 CONTINUE 83 END IF DO 230 I=1,NSI 84 85 EXC(I,I,1)=0.0D+00 86 DO 230 J=1,NSI 87 IF (J .GT. I) THEN WRITE(*, '(A22,1X,11,1X,A2,1X,11,1X,A9¥)') 88 Exchange Rate from', I, 'to', J, ' / MHz = ' 89 & READ (*, '(F10.8)') EXC(J,1,1) 90 EXC(I, J, 1) = EXC(J, I, 1) * P(1) / P(J)91 92 END IF 93 IF (I .NE. J) EXC(I,I,1)=EXC(I,I,1)-EXC(J,I,1) 94 230 CONTINUE C 95 96 C RF Strength in Frequency Units C 97 WRITE(*,'(A27¥)') 'ORF Field Strength / kHz = ' READ (*,'(F6.3)') W1 98 99 100 C С DIM(1), DIM(2) : Sampling Points in each Dimension 101 C 102 103 DO 300 I=1,2 WRITE(*,'(A13,I1)') 'ODimension : ', I WRITE(*,'(A30¥)') ' Number of Sampling Points = ' READ (*,'(I5)') DIM(I) 104 105 2 106 IF (DIM(I) .GT. MXD(I)) THEN 107 WRITE(*, '(A14)') '0 Too Large !! ' 108 109 GO TO 2 110 END IF WRITE(*,'(A35¥)') ' Time Increment (in microsec) = ' 111 READ (*, '(F5.3)') T1(1) 112 300 CONTINUE 113 С 114 RGF : Stores Computational Condition 115 C TDF : Saves FID Data 116 C

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Microsoft FORTRAN Optimizing Compiler Version 4.01 Line# Source Line 117 C WRITE(*,'(A25¥)') 'ORegistry File Name = ' READ(*,'(A15)') RGF WRITE(*,'(A25¥)') ' Time Domain File Name = ' READ(*,'(A15)') TDF 118 119 120 121 122 C ______ 123 C Get the Number to be calculated C 124 3 WRITE(*, '(A33¥)') 'ONumber of Division over THETA = ' 125 READ(*, '(13)') N 126 IF (N .GT. MXT) GOTO 3 127 128 D=DBLE(N)PID=PI1/D 129 130 DO 400 I=0,N Z(I) = DBLE(I)/D131 132 Z(-I) = -Z(I)SNT=DSQRT(1.0-Z(1)*Z(1))133 134 DO 400 J=0,N 135 X(J,1)=SNT*DCOS(PID*DBLE(J)) 136 Y(J,I)=SNT*DSIN(PID*DBLE(J)) X(-J, I) = X(J, I)137 138 Y(-J,I) = -Y(J,I)400 CONTINUE 139 WRITE(*, '(A38,15/)') 140 & ' Total Division over THETA, PHI = ',N*N*4-N*2 141 142 C C 143 Store the Parameters C 144 145 OPEN (UNIT=50, FILE=RGF, ACCESS='SEQUENTIAL') WRITE(50,'(A40)') ' ----- Computational Conditions ----- '
WRITE(50,'(/A17)') ' < Interactions >'
WRITE(50,'(A22,F8.3)') ' Lamor Freq / MHz = ', W0
WRITE(50,'(A22,F7.3)') ' RF Field / KHz = ', W1 146 147 148 149 DO 500 1=1,NSI 150 151 WRITE(50, '(/A10, 11, A16, F10.8, A2)') 152 2 . Site : ', I, ' (Population = ', P(I), ')' WRITE(50, '(A16, F6.4, A8, F6.4)') 153 ' QCC / MHz = ',QCC(I),'; ETA = ',ETA(I) WRITE(50,'(A19,F5.2,A2,F5.2,A2,F5.2)') 154 8 155 ' Euler Angles : ',ALP(I),', ',BET(I),', ',GAM(I) WRITE(50,'(A27,F6.2)') 156 & 157 158 & . Chemical Shift / kHz = ',CHS(I)*1.0D+03 159 500 CONTINUE 160 WRITE(50, '(/A25)') ' < Exchange Rates / MHz >' 161 DO 510 I=1,NSI DO 510 J=1,NSI 162 163 WRITE(50, '(4X, 11, A5, 11, F16.12)') I, '--> ', J, EXC(I, J, 1) 164 510 CONTINUE WRITE(50,'(/A16)') ' < Calculation >'
WRITE(50,'(A45)') ' Dimension Data Points Time Increments' 165 166 DO 530 I=1,2 167 WRITE(50, '(8X, 11, 10X, 13, 10X, F10.5)') I, DIM(I), TI(I) 168 169 530 CONTINUE WRITE(50, '(/A21, 13)') ' Total Division = ',N*N*4-N*2 WRITE(50, '(/A19,A15)') ' Data Stored in ',TDF 170 171 172 CLOSE (UNIT=50) 173 C 174 C Symmetrize the Exchange Matrix

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Line#	So	urce	e Line Microsoft FORTRAN Optimizing Compiler Version 4.01
175	С		and Set the Spin Density Vectors at Thermal Equilibrium
176 177 178 179 180 181 182 183 184 185 186 187	L	600	DO 600 I=1,NS1 P(I)=DSQRT(P(I)) THD(1,I)= SQ3*P(I) THD(2,I)= -P(I) THD(3,I)= 0.0D+00 THD(4,I)=-SQ3*P(I) CONTINUE DO 610 I=1,NS1 DO 610 J=1,NS1 IF (J .NE. I) EXC(J,I,1)=EXC(J,I,1)*P(I)/P(J) CONTINUE
188	С	010	Determine the Parameters suitable to Calculation
190 191 192 193 194	c		DO 620 I=1,NSI QC2(I)=PI2*QCC(I)*QCC(I)/W0*TI(2)/9.6D+01 QCC(I)=PI2*QCC(I)/8.0D+00*TI(1) ET2(I)=ETA(I)*ETA(I)
195 196 197 198 199 200 201	C	620	CHS(I)=PI2*CHS(I)*TI(2) DO 620 J=1,NSI EXC(J,1,2)=EXC(J,1,1)*TI(2) EXC(J,I,1)=EXC(J,I,1)*TI(1) CONTINUE RFS=PI2*W1*TI(1)*1.0D-03
202	C		Powder Averaging Start here
203 204 205 206 207 208 209 210 211 212 213 214	С	8 700 710	NN=0 DO 710 I=-N+1,N-1 WRITE(*,'(A30,I5)') '+ Powder Averaging Now : ',NN+N*2 DO 700 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 CONTINUE CONTINUE
215	C		Normalize and Store the Data
217 218 219 220 221 222 223	C	800	OPEN(UNIT=10,FILE=TDF) D=1.0D+00/DBLE(NN) DO 800 I=1,DIM(1) DO 800 J=1,DIM(2) WRITE(10,'(E13.7,1X,E13.7)',IOSTAT=ERS,ERR=10000) ARD(J,I)*D CONTINUE CLOSE (UNIT=10)
225	CCC		Normal End.
226	C		GO TO 99999
228 229	CC		Error Exist in the Procedure.
230 231 232	C 10	000	WRITE(*,'(A18,15)') ' File Write Error ',ERS GO TO 99999

P	A	G	E				5	
0	9	4	2	7	-	9	0	
1	9	:	3	6	:	4	7	

Line#	Source Line Microsoft FORTRAN Optimizing Compiler Version 4.01
233 234 235 236 237 238 239 240 241	20000 WRITE(*,'(A23,15)') ' Diagonalization Error ',ERS C 99999 END C BLOCK DATA 1XTO1Z COMPLEX*8 ARD(256,128) REAL*8 TDX(8),R(4),P(2) INTEGER*4 DIM(2) COMMON (ARD,ARD,DIM TDX R P
242 243 244 245 246 247 248 249 250	C Transformation Laws in Ix to Iz basis DATA R/ 6.123724356957945D-01, & 3.535533905932738D-01, & -1.060660171779821D+00, & -6.123724356957945D-01/ END \$PAGE

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Line#	Sourc	e Line Microsoft FORTRAN Optimizing Compiler Version 4.01
251 252	с	SUBROUTINE EVOLVE(L,M,X,Y,Z,ERR)
253	C	Calculate the Evolution of the Density Vectors
254 255 256 257 258 259 260 261 262 262	C	COMPLEX*8 ARD(256,128) COMPLEX*16 L1(8,8),H1(4,2,4,2),Q1(8,8),E1(8),L2(2,2),Q2(2,2),E2(2) COMPLEX*16 DZ1(2,128),RQ1(2,8),PQ2(2,2),C REAL*8 QCC(2),ETA(2),QC2(2),ET2(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,SQ3,X2,Y2,Z2,CT2,ST2,CP1 REAL*8 TDX(8),R(4),P(2),CDABSP,EPS INTEGER*4 DIM(2),1,J,K,S,S1,S2,SS,LM,ERR
263 264 265 266 267 268 269	C	EQUIVALENCE (L1,H1) PARAMETER(SQ3=8.660254037844385D-01) COMMON /PAR/QCC,ETA,QC2,ET2,CH5,RF5,EXC COMMON /ARG/SA,CA,SB,CB,SG,CG /ARD/ARD,DIM,TDX,R,P CDABSP(C)=DABS(DREAL(C))+DABS(DIMAG(C)) DATA EPS/1.0D-18/
270 271	CC	Set the Liouvillians correspond to F1 and F2 axis
272 273	С	DO 100 S=1,M
274 275	C C	Transformation of Coordinate to Molecular Frame
276 277 278 279 280 281 282 283 284 284		Z2=SB(S)*CG(S)*X+SB(S)*SG(S)*Y+CB(S)*Z X2= (CA(S)*CB(S)*CG(S)-SA(S)*SG(S))*X * (CA(S)*CB(S)*SG(S)+SA(S)*CG(S))*Y-CA(S)*SB(S)*Z Y2=-(SA(S)*CB(S)*CG(S)+CA(S)*SG(S))*X * -(SA(S)*CB(S)*SG(S)-CA(S)*CG(S))*Y+SA(S)*SB(S)*Z CT2=Z2*Z2 ST2=1.0D+00-CT2 CP1=(X2*X2-Y2*Y2)*ETA(S)
285	C	First Order Quadrupole Splitting
287	C	WQ1=QCC(S)*(CT2*3.0+CP1-1.0)
289	C	Second Order Quadrupole Shift + Chemical Shift
291 292 293 294 295	C	WQ2=CHS(S)+QC2(S) *(ST2*ST2*9(1.+CT2)*CP1*6.+CP1*CP1+ET2(S)*CT2*4. -(ST2*CT2*9.+CT2*CP1*6.0-CP1*CP1+ET2(S)*ST2)*8.0) L2(S,S)=DCMPLX(EXC(S,S,2),WQ2)
297	C	Set the Hamiltonian in the basis Ix
298 299 300 301 302 303 304 305 306 307 308	L	$ \begin{array}{l} WQ3=WQ1*SQ3 \\ XC(1,1,S)=WQ1+RFS \\ XC(1,2,S)=WQ3 \\ XC(1,3,S)=WQ3 \\ XC(1,4,S)=0.0 \\ XC(2,2,S)=-RFS \\ XC(2,3,S)=0.0 \\ XC(2,4,S)=WQ3 \\ XC(3,3,S)=RFS*3.0D+00 \\ XC(3,4,S)=WQ3 \end{array} $

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Line	Sc	ourc	Line Microsoft FORTRAN Optimizing Compiler Version 4.01
309 310 311 312	CCC	100	XC(4,4,S)=-WQ1+RFS CONTINUE Set the Liouvillan
313 314 315 316 317 318 319 320 321 322 323 324 325 326 327 328 329 330 331 332 333 334		200 210 220	DO 220 S=1,M DO 200 I=1,L H1(I,S,I,S)=DCMPLX(EXC(S,S,1),XC(I,I,S)) DO 200 J=1+1,L H1(I,S,J,S)=DCMPLX(0.0D+00,XC(I,J,S)) H1(J,S,I,S)=H1(I,S,J,S) CONTINUE DO 210 SS=S+1,M DO 210 J=1,L IF (I .EQ. J) THEN H1(I,S,I,SS)=EXC(S,SS,1) H1(I,SS,I,S)=EXC(S,SS,1) ELSE H1(I,S,J,SS)=0.0D+00 H1(J,SI,SS)=0.0D+00 H1(J,SS,I,S)=0.0D+00 H1(J,SS,I,S)=0.0D+00 END IF CONTINUE CONTINUE
335 336 337 338 339 340	С	300	DO 300 S=1,M DO 300 SS=S+1,M L2(S,SS)=EXC(S,SS,2) L2(SS,S)=EXC(S,SS,2) CONTINUE
$\begin{array}{r} 341\\ 342\\ 343\\ 344\\ 345\\ 346\\ 347\\ 348\\ 349\\ 350\\ 351\\ 352\\ 353\\ 354\\ 355\\ 356\\ 357\\ 358\\ 359\\ 360\\ 361\\ 362\\ 363\\ 365\\ 365\\ 565\\ 565\\ 566\\ 357\\ 358\\ 359\\ 360\\ 361\\ 362\\ 365\\ 365\\ 565\\ 365\\ 365\\ 365\\ 365\\ 365$	CCC	400 410 420 500	Get the Eigenvalues and Eigenvectors to Calculate Exponentials M=L*M CALL CHEQRD(LM,L1,4,E1,Q1,ERR) F (ERR .NE. 0) RETURN 00 400 I=1,LM E1(1)=CDEXP(E1(1)) ONTINUE SS=0 00 420 S=1,2 D0 410 K=1,LM RQ1(S,K)=0.0D+00 D0 410 J=1,L D0 410 I=1,LM RQ1(S,K)=RQ1(S,K)+R(J)*Q1(J+SS,K)*Q1(I,K)*TDX(I) CONTINUE SS=SS+L ONTINUE SS=SS+L ONTINUE SS=SS+L ONTINUE F (ERR .NE. 0) RETURN 00 500 I=1,M E2(I)=CDEXP(E2(I)) ONTINUE 00 S2=1 M
362 363 364 365 366		500	DO 500 I=1,M E2(I)=CDEXP(E2(I)) CONTINUE DO 510 S2=1,M DO 510 S1=1,M

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Line#	Sourc	e Line Microsoft F	CORTRAN Optimizing Compiler	Version 4.01
367 368 369 370 371	510 C	PQ2(S1,S2)=0.0D+00 DO 510 S=1,M PQ2(S1,S2)=PQ2(S1,S2)+ CONTINUE	P(S1)*Q2(S1,S2)*Q2(S,S2)	
372	C	Calculate Density Vectors	at the end of rf Pulse	
374 375 376 377 378 379 380 381	600 6	DO 600 I=1,DIM(1) DO 600 S=1,M DZ1(S,I)=0.0D+00 DO 600 J=1,LM RQ1(S,J)=RQ1(S,J)*E1(J DZ1(S,I)=DZ1(S,I)+(RQ1 CONTINUE) (S,J)-DCONJG(RQ1(S,J)))	
382	C	Calculate FID's		
383 384 385 386 387 388	C	DO 710 J=1,DIM(2) DO 700 I=1,DIM(1) DO 700 S1=1,M DO 700 S2=1,M ARD(J,I)=ARD(J,I)+PG	2(51,52)*DZ1(52,1)	
389 390 391	700	CONTINUE DO 710 S2=1,M DO 710 S1=1,M		
392 393	710	PQ2(S1,S2)=PQ2(S1,S2)* CONTINUE	E2(S2)	
394 395 396	C	RETURN		
397 398	C \$PAGE	END		

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Line#	So	urc	e Line Microsoft FORTRAN Optimizing Compiler Version 4.01
399	c		SUBROUTINE CHEQRD(N,LC,NBW,EC,VC,ERR)
400	C		Calculate the Eigenvalues and Eigenvectors of Symmetric Matrix
402 403 404	C		COMPLEX*16 LC(N,N),VC(N,N),EC(N),ZX,ZY,ZZ,ZR,ZQ,ZC,ZS REAL*8 CDABSP,DEL
405	С		INTEGER*4 I, J, K, IFI, IFM, IMI, JPM, JMI, LL, LU, M, IIK, IIKMAX, ERR
407 408 409	С		CDABSP(ZZ)=DABS(DREAL(ZZ))+DABS(DIMAG(ZZ)) DATA DEL,ITRMAX/1.0D-15,30/
410	C		Parameter Error Check
412	С		IF ((N .LE. 1) .OR. (NBW .GT. N)) GO TO 20000
414 415 416	CCC		Set the Eigenvectors to Unit Matrix and Determines the Band Width of the Matrix under Treatment.
417 418 419	C		DO 110 I=1, N DO 100 J=1, N VC(J, 1) = 0.0D+00
420		100	CONTINUE VC(1 L)=1 0D+00
422		110	CONTINUE
423			DO 130 I=1,N
425			$\frac{1}{1} \int \frac{1}{1} \int \frac{1}$
427		120	NBW=MAX0(NBW,K)
429		130	END IF
431 432 433	CCCC		Reduction of Band Width to Tridiagonal Matrix by Jacobi Rotations.
434 435 436	L		DO 270 M=NBW, 2, -1 DO 270 I=1, N-M
437 438 439			IPM=1+M IM1=IPM-1 IF (CDABSP(LC(1,IPM)), GT, DEL) THEN
440 441			ZR=-LC(1, IM1)/LC(1, IPM) ZQ=CDSQRT(1, 0D+00+ZR*ZR)
442 443			IF (CDABSP(ZQ) .LT. DEL) GOTO 30000 ZS=1.0D0/ZQ
444			DO 200 J=1,N
446 447			ZZ=LC(IM1,J) LC(IM1,J)=ZZ*ZC+LC(IPM,J)*ZS
448 449		200	LC(IPM, J)=LC(IPM, J)*ZC-ZZ*ZS CONTINUE
450 451			DO 210 $J=1, N$ ZZ=LC(J, IM1)
452			$LC(J, 1M1) = ZZ \times ZC + LC(J, 1PM) \times ZS$ $LC(J, 1PM) = LC(J, 1PM) \times ZC - ZZ \times ZS$
454 455		210	CONTINUE DO 220 J=1,N
456			ZZ = VC(J, IMI)

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Line#	S	ource	e Line Microsoft FORTRAN Optimizing Compiler Version 4.01
457 458 459		220	VC(J, 1M1)=ZZ*ZC+VC(J, 1PM)*ZS VC(J, 1PM)=VC(J, 1PM)*ZC-ZZ*ZS CONTINUE
460			JPM=J+M
462			JM1=JPM+1 IF (CDABSP(LC(J,JM1)) .GT. DEL) THEN
464			ZR = -LC(J, JPM)/LC(J, JM1) $ZQ = CDSQRT(1, 0D0 + ZR + ZR)$
466			IF (CDABSP(ZQ) .LT. DEL) GOTO 30000
467			ZS=1.0D0/ZQ ZC=-ZS*ZR
469			DO 230 $K=1, N$
471			LC(JPM, K) = ZZ * ZC + LC(JM1, K) * ZS
472		230	LC(JM1,K)=LC(JM1,K)*ZC-ZZ*ZS CONTINUE
474		200	DO 240 K=1.N
475			LC(K, JPM) = ZZ * ZC + LC(K, JM1) * ZS
477		240	LC(K, JM1)=LC(K, JM1)*ZC-ZZ*ZS
479		240	DO 250 K=1,N
480			ZZ = VC(K, J+M) VC(K, JPM) = ZZ * ZC + VC(K, JM1) * ZS
482		250	VC(K, JM1)=VC(K, JM1)*ZC-ZZ*ZS
484		200	END IF
485		260	CONTINUE END IF
487	C	270	CONTINUE
489	C		Search for a Small Sub-diagonal Element.
490	C		LU=N
492		300	ITR=0
494		320	IF (CDABSP(I.C(LL,LL-1)) .GT. DEL) THEN
495			IF (LL .GT. 1) GO TO 320
497 498			END IF IF (IL, NE, LU) THEN
499	С		16 Comparent of and Alleriand within 20 Hanshiens
501	C		Truncate the Computation.
502 503	С		IF (ITR .GT. ITRMAX) GO TO 10000
504	С		Determine the Onigin Shift of the Figenualue of the 2 by 2
506	CC		Bottom Submatrix which is Nearer to the bottom Element.
508	C		ZX=(LC(LU-1,LU-1)+LC(LU,LU))*0.5D+00
509			ZY=ZX-LC(LU,LU) ZZ=CDSQRT(LC(LU-1,LU)*LC(LU,LU-1)+ZY*ZY)
511			ZZ=DSIGN(1.0D+00, CDABSP(ZY-ZZ)-CDABSP(ZY+ZZ))*ZZ+ZX
513			ZC=1.0D+00
514			DO 360 I = LL, LU = 1

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Microsoft FORTRAN Optimizing Compiler Version 4.01 Line# Source Line 515 IP1 = 1 + 1516 C 517 C Left- and Right-hand Transformation. 518 C _____ ZX=LC(I ,I) 519 ZY=LC(IP1,I) 520 521 ZR=CDSQRT(ZX*ZX+ZY*ZY) 522 IF (CDABSP(ZR) .LT. DEL) GOTO 30000 523 LC(I,I)=ZC*ZRIF (I .GT. LL) LC(I,I-1)=ZS*ZR LC(IP1,IP1)=LC(IP1,IP1)-ZZ 524 525 ZC=ZX/ZR 526 527 ZS=ZY/ZR DO 330 J=IP1,N 528 529 ZY = LC(I, J)LC(I , J)=ZY*ZC+LC(IP1, J)*ZS 530 531 LC(IP1, J) = LC(IP1, J) * ZC - ZY * ZS532 330 CONTINUE 533 DO 340 J=1,1 534 ZY = LC(J, I)LC(J, I)=ZY*ZC+LC(J, IP1)*ZS LC(J, IP1)=LC(J, IP1)*ZC-ZY*ZS 535 536 537 340 CONTINUE 538 LC(I,I)=LC(I,I)+ZZ539 DO 350 J=1,N ZY=VC(J,I) 540 541 $VC(J, 1) = ZY \times ZC + VC(J, |P|) \times ZS$ 542 VC(J, IP1)=VC(J, IP1)*ZC-ZY*ZS 543 350 CONTINUE 544 360 CONTINUE 545 $LC(LU, L, U-1) = LC(LU, LU) \times ZS$ 546 $LC(LU, LU) = LC(LU, LU) \times ZC + ZZ$ 547 ITR=ITR+1 548 GO TO 310 549 END IF 550 LU=LU-1 551 IF (LU .GT. 1) GO TO 300 552 C -----_____ 553 C QR-Transformation is Over. 554 C Eigenvalues are Given 555 C by the Diagonal Elements of the Resultant Matrix. C 556 ----_____ 557 DO 400 I=1,N 558 EC(I)=LC(I,I)559 400 CONTINUE 560 C ------C 561 Normal Exit. 562 C 563 ERR=0 564 RETURN 565 C 566 C Error Exit. 567 C 10000 : Not Converged. 20000 : Parameter Error. 568 C 569 C 30000 : Devide by Zero. 570 C 571 10000 ERR=10000 572 RETURN

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Line# Source Line Microsoft FORTRAN Optimizing Compiler Version 4.01

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) Data size = 0000 (0) Bss size = 0000 (0)

No errors detected

