Articles

A Theoretical Representation of Relaxation Processes in Complex Spin System using Liouville Space Method

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For the study of relaxation processes in complex spin system, a general master equation, which can be used to simulate a vast range of pulse experiments, has been formulated using the Liouville representation of quantum mechanics. The state of a nonequilibrium spin system in magnetic field is described by a density vector in Liouville space and the time evolution of the system is followed by the application of a linear master operator to the density vector in this Liouville space. In this master equation the nuclear spin relaxation due to intramolecular dipolar interaction or randomly fluctuating field interaction is explicitly implemented as a relaxation supermatrix for a strong coupled two-spin (1/2) system. The whole dynamic information inherent in the spin system is thus contained in the density vector and the master operator. The radiofrequency pulses are applied in the same space by corresponding unitary rotational supertransformations of the density vector. If the resulting FID is analytically Fourier transformed, it is possible to represent the final nonstationary spectrum using a frequency dependent spectral vector and intensity determining shape vector. The overall algorithm including relaxation interactions is then translated into an ANSI FORTRAN computer program, which can simulate a variety of two dimensional spectra. Furthermore a new strategy is tested by simulation of multiple quantum signals to differentiate the two relaxation interaction types.

Introduction

The density matrix theory, originally introduced to describe statistical concepts in quantum mechanics[1], is the most powerful tool for the theoretical calculation of spectra. A complex spin system described by the density matrix σ_{ij} is said to be in superposition state of basis vector ϕ_i and ϕ_j, which spans the corresponding Hilbert space[2]. If the system is in equilibrium in the magnetic field, the density matrix is diagonal and the diagonal element σ_{ii} gives statistical information about the spin population in the i-th energy level.

In the majority of modern pulse experiments in one and two dimensional NMR spectroscopy, the spin system experiencing more than one radiofrequency pulse with some time intervals will be brought into a nonequilibrium state. In this case all the possible offdiagonal elements $\sigma_{ij}(t)$, the general p-quantum coherences, can be generated, where the order of coherence p denotes the difference in total magnetic quantum number of ϕ_i and ϕ_j. The time dependence of each coherences are also interrelated, because the individual elements can be transferred to each other due to the coherence mixing effect of radiofrequency pulses. The explicit treatment of time evolution of these elements, whether they are direct observable or not, is therefore of central importance in two dimensional spectroscopy especially and even in one dimensional multipulse experiments. The density matrix in Hilbert space, however, is not the suitable choice for the explicit formulation of dynamic processes in general spin system. Particularly the derivation of nonexponential behavior of spin relaxation can only be handled indirectly over a cumbersome multiple commutator of hamiltonian[3] and density matrix in

this space or in some publications only single quantum coherences would be selected and treated seperately for a simplified spin system[4], while the other elements are completely discriminated at the expence of some part of informations.

For a complete and general treatment of this problem the Liouville space formalism[5] provides the proper solution. This method is known to be ideal for the formulation of the time dependence of the spectroscopical system, especially the spin relaxation phenomena. Instead of arranging the elements σ_{ij} in a square form of matrix in Hilbert space, they can be defined as components of a density vecotr ρ in the corresponding Liouville space. The hamiltonian can then be consistently transformed to the liouvillian superoperator, whose eigenvalues represent the direct observable quantities, the transition frequencies and intensities. The conceptual and formal distinction between the Hilbert and Liouville space method are well documented by Banwell[6] and Binsch[7], who themselves utilized the Liouville formalism to develope 'direct method' for calculation of steady state NMR spectra[8].

Recently Szymanski *et al.*[9] were capable to seperate the time dependent hamiltonian to a liouvillian superoperator for 'system of interest' and a semiclassical interaction hamiltonian between the 'system of interest' and its 'thermal bath', from which a relaxation superoperator in its full dimension could be derived in this formalism. In fact, the matrix elements of the relaxation operator describes the nonexponential behavior of corresponding coherences and thus limitation of the Bloch's simple notation of 'longitudinal' and 'transversal' relaxation parameters can be overcome in this representation.

We have made use of this representation to show how the total dynamic effect can be compressed in the FID of

multipulse experiments without loss of any relaxation information of the system. For the numerical calculation of the resulting nonstationary spectra we have introduced the concept of 'spectral vector' and 'shape vector', which are originally defined and utilized by Binsch[8] for single pulse steady state spectra. Two different interaction types, the intramolecular dipolar and random fluctuating field interactions, which are mainly responsible for the spin relaxation in solution NMR, are explicitly investigated for strongly coupled two-spin (1/2) system. The overall algorithm was then translated into an ANSI FORTRAN computer program CANDYS, which can be used to simulate the effects of arbitrary pulse sequences and visualize them in 2D spectra. In addition a strategy to differentiate the two interaction types is tested by a simulation, in which the dissipation pattern of single and double quantum signals are explicitly compared.

Spin Dynamics

Basic Notations. The spin system is defined in this paper as n identical nuclei with spin quantum number 1/2 and magnetogyric ratio γ. In a static magnetic field H_o the state of the system is normally represented by an ensemble-averaged density matrix σ in a $N = 2^n$ dimensional Hilbert space. As starting point of this work we follow the general convention of representing the equilibrium density matrix elements σ_{ii} as eigenvalues of total spin operator F_z to the corresponding spin product functions ϕ_i[10]. The high resolution spin hamiltonian H^s in the frame rotating about z axis with frequencey ν has the form

$$H^s = -\sum_m^n (\nu_m - \nu) I_{zm} + \sum_{m<m'}^{n,n} J_{mm'} I_m I_{m'} \tag{1}$$

where ν, J and I are the chemical shifts (Hz), the coupling constants (Hz) and the spin operator, respectively. H^s is defined in unit of h.

The N^2 matrix elements of σ can then be declared as components of a density vector ρ in the N^2 dimensional Liouville space[5-7]. The hamiltonian will then be reformulated as liouville superoperator L.

$$L = H^s \otimes E - E \otimes H^{s*} \tag{2}$$

where E is the corresponding unit matrix and the $N^2 \times N^2$ matrix elements of L is constructed as

$$L_{ijkl} = H^s_{ik} \delta_{jl} - \delta_{ik} H^s_{lj} \tag{3}$$

In this convention the commutator in Hilbert space will be a simple scalar product of the two operators in Liouville space. The eigenvalues of the hamiltonian H^s are energy levels of the system, to which we have no direct access, whereas the eigenvalues of the liouvillian L is the differences of the energy levels and consequently direct measurable *real* quantities. An observable of A will be calculated as expectation value from the scalar product of the density vector ρ and vector operator A,

$$\langle A \rangle = A^T \rho(t) \tag{4}$$

where A^T and $\rho(t)$ are defined as the *row vector* and *column vector* (in the notation by Jeener[11] 'superbra' and 'superket'), respectively. The N^2 elements of a vector operator

must be consistently arranged in the was analogous to density vector. Any unitary operator U in Hilbert space can be transferred to an unitary superoperator U *via* simple tensor product with the complex cojugate U^*.

$$U = U \otimes U^* \tag{5}$$

We do not try to compare the relevance of each vector or supermatrix elements and regardless of the irrelevance of some elements, the equation of motion in its full dimension of Liouville space will be adopted in this work.

$$\frac{d\rho(t)}{dt} = -i L \rho(t) + R\{\rho(t) - \rho_o\} \tag{6}$$

Relaxation Operator. The general form of semiclassical model of interaction hamiltonian $H^I(t)$ is given as

$$H^I(t) = \sum_m \sum_{\mu=\lambda}^{\lambda} (-1)^\mu S_{m\mu} B_{m-\mu}(t) \tag{7}$$

where the bath operator $B(t)$ describes the time dependence of the 'classical' bath and will be replaced by stationary random functions. The irreducible spherical tensor operator S with rank λ has $2\lambda + 1$ components, $\mu = 0, \pm 1, \cdots \pm \lambda$, whereas the index m labels the interaction tensors. The relaxation superoperator, consistantly translated by Szymanski et al.[9] from this interaction Hamiltonian, will be adopted in the following work as the form

$$R = -\sum_m \sum_{m'} \sum_\mu \sum_{\mu'} \delta_{\mu\mu'} \{S_{m\mu} S_{m' \mu'} + S_{m' \mu'} S_{m\mu}\} J_{mm' \mu'} (-\omega_o\mu) \tag{8}$$

where ω_o is the mean Larmor frequency of the spins in system. The derivation superoperator S can be well derived from spherical tensor S in the same manner as in Eq. (3).

$$S_{m\mu, ijkl} = S_{m\mu, ik} \delta_{jl} - \delta_{ik} S_{m\mu, lj} \tag{9}$$

The spectral Jensity J

$$J_{mm'\mu}(\omega) = 1/2 \int_{-\infty}^{\infty} C_{mm'\mu}(\tau) \exp(-i\omega\tau) d\tau \tag{10}$$

is the Fourier transform of the classical ensemble-averaged correlation function of the bath fuctions.

$$C_{mm'\mu}(\tau) = \{B_{m\mu}(0)B_{m'\mu}(-\tau)\}_{av} \tag{11}$$

For the numerical calculation a further simplification of Eq. (17) must be introduced here. As the best alternative[12] for the explicit form the correlation function $C(\tau)$ is divided into a time-independent term $C(0)$ and an index-independent term $g(\tau)$

$$C_{mm'\mu}(\tau) = C_{mm'\mu}(0) g(\tau) = \{B_{m\mu}(0)B_{m'\mu}(0)\}_{av} g(\tau) \tag{12}$$

The limiting conditions from the molecular dynamics

$$g(\tau) \cong 1 \quad \text{for } |\tau| \ll \tau_c$$
$$\cong 0 \qquad |\tau| \gg \tau_c$$

allow us to express the function $g(\tau)$ as an exponential function.

$$g(\tau) = \exp(-|\tau|/\tau_o) \tag{13}$$

And thus the exact form of the correlation time τ_c can be defined

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And thus the exact form of the correlation time τ_c can be defined

$$\tau_c = \int_0^\infty g(\tau)\, d\tau \tag{14}$$

Making use of Eq. (12) and (13) the spectral density will be rewritten

$$J_{mm'\mu}(\omega) = \frac{1}{2}\{B_{m\mu}(0)\, B_{m'-\mu}(0)\}_{av} \int_{-\infty}^\infty \exp\{(-|\tau| - i\,\omega\tau_c\tau)/\tau_o\}\, d\tau \tag{15}$$

In high resolution NMR spectrum the condition of extreme narrpwomg. $\omega\tau_c \ll 1$, is normally satisfied and the integration term in Eq. (15) can be replaced with $2\tau_c$.

$$J_{mm'\mu} = \{B_{m\mu}(0)B_{m'-\mu}(0)\}_{av}\,\tau_c \tag{16}$$

In the following we will describe how the spin operator in Eq. (9) and the function for spectral density Eq. (16) can be described in relation to a specific interaction type for the construction of the complete form of relaxation superoperator.

Intramolecular Dipolar Interaction. This type of interaction concerns a mutual influence between the two coupled spins A and B and the spin operators are given[9] by

$$S_{mo} = \frac{1}{2\sqrt{6}}\{4\, I_z^A I_z^B - (I_+^A I_-^B + I_-^A I_+^B)\},$$

$$S_{m+1} = \mp\frac{1}{2}(I_z^A I_\pm^B + I_\pm^A I_z^B),$$

$$S_{m\pm2} = \frac{1}{2} I_\pm^A\, I_\pm^B \tag{17}$$

and the spherical tensor components of the random bath function have the form[13]

$$B_0(t) = \frac{\sqrt{3}}{4}a\{1 - 3\cos^2\theta(t),$$

$$B_1(t) = \frac{3}{2\sqrt{2}}a[\sin\theta(t)\,\cos\theta(t)\,\exp\{-i\,\varphi(t)\}],$$

$$B_2(t) = \frac{3}{4\sqrt{2}}a[\sin^2\theta(t)\,\exp\{-2\,i\,\varphi(t)\}] \tag{18}$$

where $a = h\gamma^2/b^3$ and b is the distance between the two mutually interaction spins. After an average of the function $B(t)$ over the random molecular motion[14]

$$\{B_0^2\}_{av} = \{B_1^2\}_{av} = \{B_2^2\}_{av} = \frac{3}{20}a^2 \tag{19}$$

the spectral density in Eq. (16) lose its index and therefore can be redefined as *relaxation rate r^D*

$$J_{mm'\mu}^D = \frac{3}{20}\,a^2\,\tau_c \equiv r^D \tag{20}$$

After substitution of the spectral density in Eq. (8) with Eq. (20) one gets the following expression for the relaxation superoperator R^D due to the dipolar interaction.

$$R^D = -r^D \sum_m \sum_{m'} \sum_\mu \sum_{\mu'} \delta_{\mu\mu'}\{S_{m\mu}S_{m'-\mu'} + S_{m'-\mu'}S_{n;\mu}\} \tag{21}$$

Random Fluctuating Field Interaction. If the relaxation of the system originates from the randomly fluctuating magnetic field H produced at the spin sites by other magnetic moments, for example other nuclei or paramagnetic spe-

cies in the sample, the spin operator S for Eq. (9) and bath function $B(t)$ for Eq. (16) can be described

$$S_{mo} = I_z,\quad S_{m\pm1} = \mp\frac{1}{\sqrt{2}}I_\pm \tag{22}$$

$$B_{mo} = -\frac{1}{\sqrt{2}}\gamma(H_z)_m,\quad B_{m\pm} = -\frac{1}{2}\gamma(H_\pm)_m \tag{23}$$

For the evaluatiun of the ensemble averages it is assumed that[15]

$$\{(H_z)^2\}_{av} = \frac{1}{3}\{(H)^2\}_{av},\quad \{(H_\pm)^2\}_{av} = \frac{2}{3}\{(H)^2\}_{av} \tag{24}$$

And thus the bath function can be written as a function of random field components.

$$\{B_{mo}B_{m'o}\}_{av} = \{B_{m\pm}B_{m'\pm}\}_{av} = \frac{1}{6}\gamma^2\{H_m H_{m'}\}_{av} \tag{25}$$

In a special case, where the random fields at the spin site m and m' are identical,

$$\{H^2\}_{av} = \{H_m H_m\}_{av} = \{H_{m'}H_{m'}\}_{av} \tag{26}$$

and because of the cross term between spin m and m', we may introduce a *correlation constant* $\varepsilon_{mm'}$ by the relation

$$\varepsilon_{mm'} = \frac{\{H_m H_{m'}\}_{av}}{\{H^2\}_{av}},\qquad \begin{array}{l}\varepsilon_{mm'} = 1 \quad \text{for } m = m'\\ 0 \le \varepsilon_{mm'} \le 1 \quad \text{for } m \ne m'\end{array} \tag{27}$$

which describes the complete correlation ($\varepsilon_{mm'} = 1$) or uncorrelation ($\varepsilon_{mm'} = 0$) of the fluctuating fields at each nuclear sites m and m'.

$$J_{mm'}^R = \frac{1}{6}\gamma^2\tau_c\{H^2\}_{av}\,\varepsilon_{mm'} \equiv r^R\,\varepsilon_{mm'} \tag{28}$$

where we have defined the *relaxation rate r^R* due to the random field interaction. The relaxation superoperator R^R is thus constructed as

$$R^R = -r^R \sum_m \sum_{m'} \sum_\mu \sum_{\mu'} \delta_{\mu\mu'}\{S_{m\mu}S_{m'-\mu'} + S_{m'-\mu'}S_{m\mu}\}\,\varepsilon_{mm'} \tag{29}$$

The spectral densities in Eq. (20) in Eq. (28) are completely reduced to the relaxation rate r^D and r^R and can be interpreted as purely phenomenological parameter for the related interaction types. The resulting matrix elements of R represent the comple nonexponential behavior of all the individual coherences. Although in case of certain special experimental situations the 'intrinsic' and 'extrinsic' symmetry properties can allow us to rationalize some of the $N^2 \times N^2$ matrix elements[9], we make use of all the matrix elements to handle the general pulse sequences.

Radiofrequency Pulse Operator. If a nonselective strong RF pulse with the field strength H_1, which lies vertical to the static field, acts on the spin system, the RF field causes change in spin state. In the rotating coordinate system this means that the pulse with pulse duration τ' brings the total magnetisation vector α degree ($\alpha = \tau\gamma H_1$) in direction to yz-plane (or xz-plane), if the field lies on the x-axis (or y-axis). Since the intensity of the RF field is normally high enough, that the time evolution of the system during the short pulse can be ignored. In theoretical words, the act of RF pulse can be expressed as a rotation operation of the density matrix,

$$\sigma + (t) = P + (\alpha)\ \sigma - (t)\ P - (\alpha) \tag{30}$$

where $\sigma - (t)$ and $\sigma + (t)$ represnt the system before and after the pulse operation. The rotation operator $P(\alpha)$ in Hilbert space can be formulated[16] using the corresponding spin operator.

$$P_\pm(\alpha_x) = \prod_m^n \{\exp(\pm i\ \alpha\ I_{xm})\} = \prod_m^n \{\cos(\alpha/2) \pm 2i\ \sin(\alpha/2)\ I_{xm}\},$$

$$P_\pm(\alpha_y) = \prod_m^n \{\exp(\pm i\ \alpha\ I_{ym})\} = \prod_m^n \{\cos(\alpha/2) \pm 2i\ \sin(\alpha/2)\ I_{ym}\}, \tag{31}$$

from which the corresponding rotation superoperator is constructed *via* Eq. (5)

$$P(\alpha) = P + (\alpha)\ \otimes\ P - (\alpha) \tag{32}$$

The operation in Eq. (30) has more compact form in Liouville space

$$\rho + (t) = P(\alpha)\ \rho - (t) \tag{33}$$

Master Equation. The equation of motion of the system in nonequilibrium state can be thus formulated using Eq. (2) and (21) or (29) in Liouville space.

$$\frac{d\ \rho(t)}{dt} = -i\ L\ \rho(t) + R\{\rho(t) - \rho_o\} \tag{34}$$

Owing to the operation invariance of ρ_o towards L the Eq. (34) can be rewritten to

$$\frac{d\ \rho(t)}{dt} = \{-i\ L + R\}\ \{\rho(t) - \rho_o\} \tag{35}$$

For the operator and density vector new notations are introduced here; the master operator

$$M(\nu,\ J,\ r) = -i\ L(\nu,\ J) + R(r) \tag{36}$$

as a function of chemical shifts (ν), coupling constants (J) and relaxation rate (r), and the deviation density vector for the system in nonequilibrium state.

$$\eta(t) = \rho(t) - \rho_o \tag{37}$$

The compact form of differential equation

$$\frac{d\ \eta(t)}{dt} = M\eta\ (t) \tag{38}$$

gives the solution

$$\eta(t) = \exp(M\ t)\ \eta(t_o) \tag{39}$$

The symmetric complex matrix operator M can be diagonalised using the complex orthogonal eigenvecotor $V^{17,18}$,

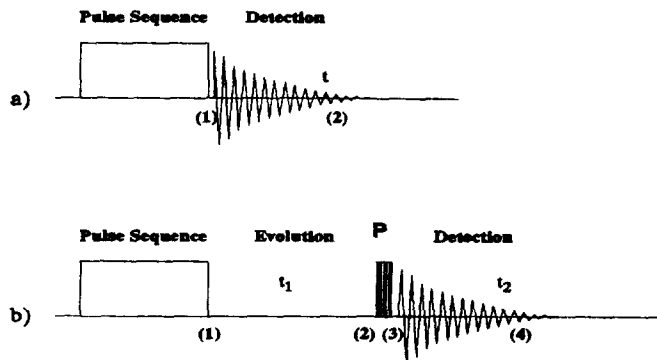$$\Lambda_{diag} = V^{-1}MV,\ M = V\Lambda_{diag}V^{-1} \tag{40}$$

in which the inverse V^{-1} and the complex diagonal matrix D can be transformed from the transpose of orthogonal but not unitary matix V^{19}.

$$V^{-1} = D^{-1}V^T,\ D = V^T V \tag{41}$$

The final master equation of motion is formulated

$$\eta(t) = V \exp(\Lambda\ t)\ V^{-1}\eta(t_o) \tag{42}$$

and the diagonal exponential operator is

Figure 1. Schematic representation of pulse experiments for (a) $1D$ spectroscopy and (b) $2D$ spectroscopy. The density vector in the detection period can be successively reduced to the density vector $\rho(t_o)$ and $\eta(t_o)$ immediately after the pulse sequence using master and/or pulse operator.

$$\exp(\Lambda t) = diag.\{\exp(\lambda_1 t),\ \exp(\lambda_2 t),\ \cdots\ \exp(\lambda_N t)\} \tag{43}$$

Spectral Synthesis

Calculation Algorithm. A general multipulse experiment can be interpreted in this context as alternating operations of the RF pulse operator and the time devloping master operator. The final signal acquisition process will be performed by the projection operator, which is mentioned below. The general procedure to simulate pulse experiments with this algorithm is described in Figure 1.

When the pulse sequence is properly designed for the purpose of the experiment, the density vector $\rho(t_o)$ and $\eta(t_o)$ at the moment (1) just after the pulse sequence can be calculated using master operator and corresponding pulse operator. The system in detection period, $\eta(t)$, can be then easily reduced to the density vector $\eta(t_o)$. This means in the case of $1D$ spectroscopy (Figure 1(a)) for each numbered state;

(1): $\eta(t_o) = \rho(t_o) - \rho_o$

(2): $\eta(t) = \exp(M\ t)\ \eta(t_o)$

The free induction decay (FID) $G(t)$ is then interpreted as the interaction between the density vector and the projection vector operator

$$G(t) = -i\ F_+^T\ \eta(t) = -i\ F_+^T\ \exp(M\ t)\eta(t_o) \tag{44}$$

where F_+ is the vector operator formed consistantly from the matrix elements of the operator $F_+ = \Sigma I_+$ and selects the single quantum coherences from the density vector $\eta(t)$. The frequency spectrum $S(\omega)$, where $\omega = 2\pi\nu$, is defined as the Fourier transform of the time spectrum $G(t)$ and further reduced to the fundamental terms, $\eta(t_o)$, and eigenvalue Λ and eigenvector V of the master operator.

$$S(\omega) = \int_0^\infty G(t)\ \exp(-i\ \omega\ t)\ dt$$

$$= \int_0^\infty \{-i\ F_+^T\ \exp(M\ t)\ \eta(t_o)\ \exp(-i\ \omega\ t)\}\ dt$$

$$= -i\ F_+^T\ V\{\int_0^\infty \exp(\Lambda\ t)\ \exp(-i\ \omega\ t)\ dt\}V^{-1}\eta(t_o) \tag{45}$$

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The integral term in Eq. (45) has an analytical solution in closed form and there is a reason to introduce a new *spectral vector* $Q(\omega)$ by the definition;

$$\int_0^\infty \exp\{(\Lambda - i\,\omega)t\}dt = -(\Lambda - i\,\omega)^{-1} \equiv Q(\omega) \qquad (46)$$

and *vector operator* A and *shape vector* B;

$$A^T \equiv -i\,F_+^T\,V, \quad B \equiv V^{-1}\eta(t_o) \qquad (47)$$

The final $1D$ spectrum $S(\omega)$ is thus a simple product *frequency-determining* spectral vector Q, *intensity-determining* shape vector B and projection vector operator A

$$S(\omega) = A^T\{Q(\omega) \otimes B\} \qquad (48)$$

where the tensor product $\{Q(\omega) \otimes B\}$ gives also a vector with the elements $q_i\,b_i$. The real and imaginary part of the shape vector give informations about the relative intensity of the x-component and y-component of the coherence respectively, and the real and imaginary parts of the spectral vector about the line broadening and line position, *i.e.*, resonance frequency, respectively. Consequently the resulting complex spectrum has also the real and imaginary part, which represent the absorption mode and dispersion mode spectrum in case of a single pulse experiment.

For $2D$ spectroscopy (Figure 1(b)) the same procedure can be summarised as follows.

(1): $\eta(t_o) = \rho(t_o) - \rho_o$

(2): $\eta(t_1) = \exp(M\,t_1)\,\eta(t_o)$

$\rho(t_1) = \exp(M\,t_1)\,\eta(t_o) + \rho_o$

(3): $\rho(t_1,\,0) = P(\alpha)\rho(t_1) = P(\alpha)\{\exp(M\,t_1)\,\eta(t_o) + \rho_o\}$

$\eta(t_1,\,0) = P(\alpha)\{\exp(M\,t_1)\,\eta(t_o) + \rho_o\} - \rho_o$

(4): $\eta(t_1,\,t_2) = \exp(M\,t_2)\,\eta(t_1,\,0)$

$= \exp(M\,t_2)\,P(\alpha)\{\exp(M\,t_1)\eta(t_o) + \rho_o\}$

$- \exp(M\,t_2)\,\rho_o$

Making use of Eq. (40) the density vector $\eta(t_1,\,t_2)$ in the detection phase becomes

$$\eta(t_1,\,t_2) = V\exp(\Lambda\,t_2)\{P'(\alpha)\exp(\Lambda\,t_1)\,B + C\} \qquad (49)$$

with the matrix operators and shape vectors B and C

$$P'(\alpha) = V^{-1}P(\alpha)\,V, \quad P''(\alpha) = V^{-1}P(\alpha) \qquad (50)$$

$$B = V^{-1}\eta(t_o), \quad C = P''(\alpha)\rho_o \qquad (51)$$

The FID is therefore

$G(t_1,\,t_2) = -i\,F_+^T\eta(t_1,\,t_2)$

$= A^T\exp(\Lambda\,t_2)\{P'(\alpha)\exp(\Lambda\,t_1)\,B + C\} \qquad (52)$

and the Fourier transformation of the function $G(t_1,\,t_2)$ about t_1 and t_2 produces the frequency spectrum $S(\omega_1,\,\omega_2)$

$S(\omega_1,\,\omega_2) = \int_0^\infty \exp(-i\,\omega_2 t_2)\int_0^\infty G(t_1,\,t_2)\exp(-i\,\omega_1 t_1)\,dt_1\,dt_2$

$= A^T\int_0^\infty \exp\{(\Lambda - i\,\omega_2)t_2\}dt_2[P'(\alpha)\int_0^\infty \exp\{(\Lambda - i\,\omega_1)t_1\}dt_1\,B$

$+ \int_0^\infty \exp(-i\,\omega_1 t_1)\,dt_1\,C] \qquad (53)$

Replacing the integration terms with the new spectral vector

components defined as

$$\int_0^\infty \exp\{(\Lambda - i\,\omega_2)t_2\}dt_2 = -(\Lambda - i\,\omega_2)^{-1} \equiv Q(\omega_2)$$

$$\int_0^\infty \exp\{(\Lambda - i\,\omega_1)t_1\}dt_1 = -(\Lambda - i\,\omega_1)^{-1} \equiv Q(\omega_1)$$

$$\int_0^\infty \exp\{(-i\,\omega_1 t_1)dt_1 = -(-i\,\omega_1)^{-1} \equiv Q_o(\omega_1) \qquad (54)$$

gives the final $2D$ spectrum

$$S(\omega_1,\,\omega_2) = A^T\{Q(\omega_2) \otimes [P'(\alpha)\{Q(\omega_1) \otimes B\} + E\{Q_o(\omega_1) \otimes C\}]\} \qquad (55)$$

The last term $E\{Q_o(\omega_1) \otimes C\}$ with the unit matrix E in Liouville space contributes only to axial signals in f_2 axis $(\omega_1 \cong 0)$. If one takes an interest only in relevant range $(\omega_1 \neq 0,\,\omega_2 \neq 0)$, the Eq. (55) can be further abbreviated to

$$S(\omega_1,\,\omega_2) = A^T\{Q(\omega_2) \otimes [P'(\alpha)\{Q(\omega_1) \otimes B\}]\} \qquad (56)$$

As the final consequence of the master operator Eq. (36) the complex spectrum $S(\omega_1,\,\omega_2)$ has mathematically the real and imaginary part as defined

$$S_r = Re\{S(\omega_1,\,\omega_2)\}, \quad S_i = I_m\{S(\omega_1,\,\omega_2)\} \qquad (57)$$

In contrast to $1D$ spectrum one cannot speak of an absorption or dispersion mode over the entire range. A *pseudo-absorption* spectrum can be attained by the combination of S_r and S_i either of the two forms;

$$S_{power} = \{S_r^2 + S_i^2\} \qquad (58)$$

$$S_{absolute} = \{S_r^2 + S_i^2\}^{1/2} \qquad (59)$$

The individual signals in these representations give information about the relative magnitudes of the related coherences. Introduction of a new vector F_1 in f_1 domain and F_2 in f_2 domain

$$F_1(\omega_1) = P'(\alpha)\{Q(\omega_1) \otimes B\}, \quad F_2(\omega_2) = Q(\omega_2) \qquad (60)$$
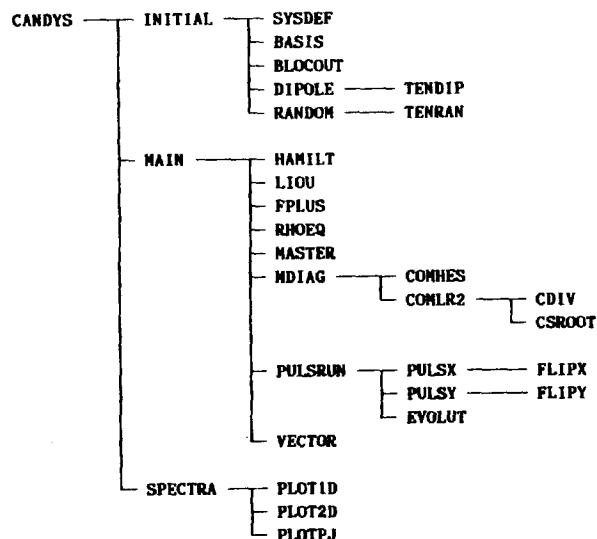
makes possible to describe $S(\omega_1,\,\omega_2)$ as

$$S(\omega_1,\,\omega_2) = S(F_1,\,F_2) = A^T\{F_2(\omega_2) \otimes F_1(\omega_1)\} \qquad (61)$$

and one obtains the individual phase information by selecting the real (F^r) or imaginary part (F^i) of the component vectors

$S_{rr} = S(F_1^r,\,F_2^r), \quad S_{ii} = S(F_1^i,\,F_2^i),$

$S_{ri} = S(F_1^r,\,F_2^i), \quad S_{ir} = S(F_1^i,\,F_2^r), \qquad (62)$

Whether or which of them in Eq. (57) and (62) produces a pure phase, *i.e.*, pure absorption or dispersion form, or a mixed phase[20] spectrum depends clearly on the composition of the pulse sequence and their phase relation to the observation pulse.

Computer Program. The developed algorithm is then translated into a computer program, which can simulate arbitrary pulse experiments and synthesise the resulting nonstationary spectra. The first version of this program is written in ANSI FORTRAN for a general 2-spin(1/2) system and named as CANDYS for Calculation Algorithm for Nonstationary Dynamic Spectrum. The structure and subroutine hierarchy of the program is shown in Scheme 1, which gives a short overview in the grogramming strategy. Three master subroutines INITIAL, MAIN and SPECTRA monitor the logi-

```
CANDYS ──┬─ INITIAL ──┬─ SYSDEF
         │            ├─ BASIS
         │            ├─ BLOCOUT
         │            ├─ DIPOLE ──── TENDIP
         │            └─ RANDOM ──── TENRAN
         │
         ├─ MAIN ──────┬─ HAMILT
         │            ├─ LIOU
         │            ├─ FPLUS
         │            ├─ RHOEQ
         │            ├─ MASTER
         │            ├─ MDIAG ──┬─ COMHES
         │            │          └─ COMLR2 ──┬─ CDIV
         │            │                      └─ CSROOT
         │            │
         │            ├─ PULSRUN ──┬─ PULSX ──── FLIPX
         │            │            ├─ PULSY ──── FLIPY
         │            │            └─ EVOLUT
         │            └─ VECTOR
         │
         └─ SPECTRA ──┬─ PLOT1D
                      ├─ PLOT2D
                      └─ PLOTPJ
```

Scheme 1. The subroutine hierarchy in program CANDYS.

cal flow by calling the corresponding subroutines and in the following some important remarks are given about the functions of each routine.

The subroutine SYSDEF reads in and prints out the input data of the spin system at hand. The input data includes the static NMR parameters (chemical shifts and coupling constants for the hamiltonian in Eq. (1)), dynamic parameters (relaxation rate in Eq. (20) or (28) and correlation constant in Eq. (27)) and the spectral parameter, such as spectral range and the digital resolution for the calculation of spectra. The input number of spins(n) will be used to calculate the dimension of the Hilbert(2^n) and Liouville(2^{2n}) space. The routine BASIS generates the spin product basis functions as eigenfunction of I_z and arranges them in the order according to their totasl F_z components. In the subroutine BLOCOUT the numbering of the basis functions and matrix elements is created and stored in an index vector, which enables the consistent transformation of a vector or matrix operator from Hilbert to Liouville space. The subroutine DIPOLE and RANDOM build up the dipolar relaxation operator in Eq. (21) and random field relaxation operator in Eq. (29) from the spin operator prepared in the routines TENDIP and TENRAN. The subroutine HAMILT sets up the hamiltonian matrix elements according to Eq. (1) using chemical shifts and coupling constants read in SYSDEF, whereas the routine LIOU converts the hamiltonian to the liouvillian superoperator in Eq. (3) with the help of the index vector. In the routine FPLUS the vector operator F_+ will be generated from the corresponding raising operator $F_+ = \Sigma I_+$. The subroutine RHOEQ calculates the diagonal elements of the equilibrium density matrix in Hilbert space using the z components of the spin operator F_z, while the offdiagonal elements are set zero and all of the matrix elements are then arranged in an one dimensional array, *i.e.*, density vector. In the subroutine MASTER the liouvillian as imaginary part from LIOU and the relaxation superoperator as real part from DIPOLE and/or RANDOM are combined to a total master operator in Eq. (36). The subroutine MDIAG controls diagonalisation of the complex and symmetric master opera-

tor by calling the subroutines COMHES and COMLR2[21]. The routine COMHES reduces the matrix into an upper Hessenberg form by the similarity transformation[17] and the routine COMLR2 finds the eigenvalue Λ and eigenvector V in Eq. (40) from this matrix by the modified LR mehod[18], while the routine CDIV and CSROOT perform complex division and complex square root. The subroutine MDIAG calculates finally the complex diagonal matrix from the eigenvector V using Eq. (41). A pulse sequence can be interpreted as alternating pulse operations and time evolutions, which will be carried out in the subroutine PULSRUN. It calls the routine PULSX or PULSY for rotation operation in Eq. (33) about x or y axis, while the corresponding pulse operator in Eq. (31) and (32) with the specified flip angles are generated in the routine FLIPX or FLIPY. The time evolution during intervals between the pulses will be calculated by the equation of motion in Eq. (39) in the subroutine EVOLUT. The subroutine VECTOR generates the spectral vectors in Eq. (46) and (54), shape vectors in Eq. (47) and (51) and matrix operator in Eq. (50). The master subroutine SPECTRA monitors the output mode of the resulting spectra according to the representatins in Eq. (57), (58), (59), and (62) as demanded in input data. In case of $1D$ experiments the spectrum will be output as $\{X_{frequency}, Y_{intensity}\}$ coordinates in the subroutine PLOT1D, while the $2D$ spectrum will be defined in theree diensional data space and output as $(X_{frequency1}, Y_{frequency2}, Z_{intensity}\}$ coordinates in PLOT2D. In the routine PLOTPJ a $2D$ spectrum can be projected in f_1 and f_2 domains and output as $1D$ representation, $\{X_{frequency1}, Y_{intensity}\}$ and $\{X_{frequency2}, Y_{intensity}\}$.

The program is compiled by the Microsoft FORTAN Version 5.0 under MS-DOS operating system and runs at IBM compatible personal computer. For the program execution the properly formulated input file must be combined and the result of a calculation, spectral data points, may be stored as output file in ASCII format. The graphical presentation of the spectra can then be performed using the commercially available programs.

Relaxation of Multiquantum Signals

By simulation of multiquantum $2D$ spectra on an artificial AB spin system we demenstrate here how two relaxation mechanisms, implemented above, can be identified. The AB spin system with the static parameters, $\nu_A = 30.0$ Hz, $\nu_B = 70.0$ Hz and $J_{AB} = 10.0$ Hz, is assumed to relax purely due to the intramolecular dipolar interaction with rate $r^D = 1.0$ Hz in one simulation and to radomly fluctuating field near the nuclear site with rate $r^R = 1.0$ Hz in the other case. In the later case a perfect correlation of the random fields at each nuclear sites is also assumed ($\varepsilon = 1.0$). To utilize the fact, that not only the relaxation behaviors of the p-quantum coherences themselves but also the relative rate between the multiple and single coherences depend on the interaction types, we decided to choose a general method to observe all the coherences of the system simultancously.
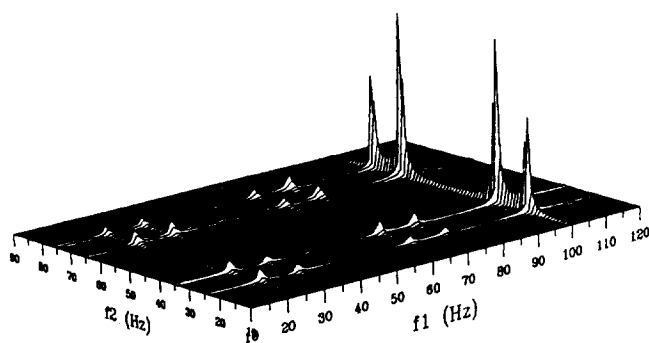
The most simple method to generate p-quantum coherences is the application of two 90° pulses seperated by a time interval τ, as shown in Figures 2(a). The single quantum coherences, transversal magnetisation, created by the first
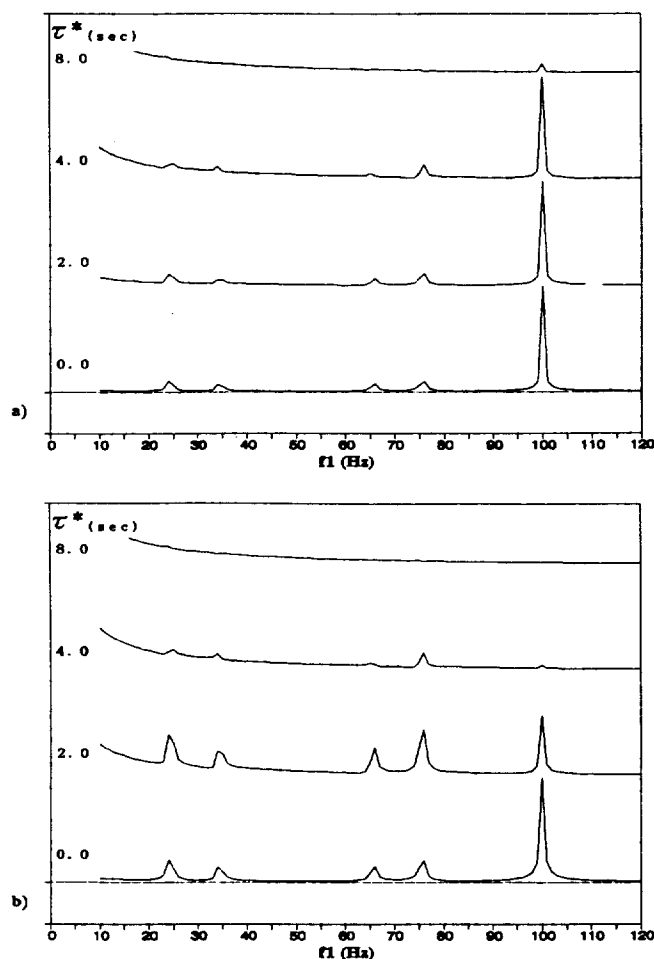
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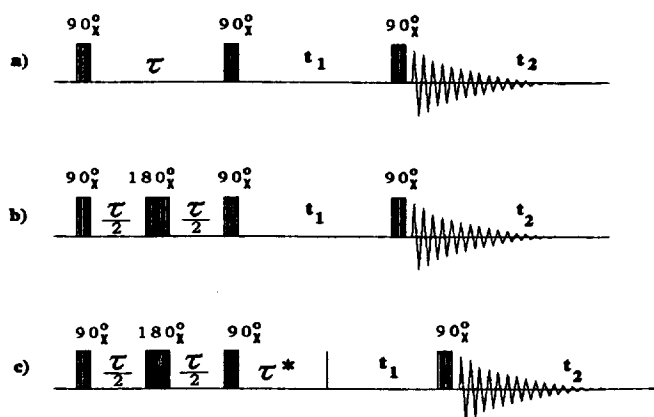
Figure 2. Pulse sequences for multiquantum $2D$ experiments: By the sequence in (a) all p-quantum coherences will be generated, while in (b) only the single and double quantum signals can be observed. The additional delay τ^* in (c) enables us to distinguish the interaction types in the relative intensities of the single and double quantum coherences.

Figure 3. A multiquantum $2D$ spectrum simulated with the pulse sequence in Figure 2(b). The chemical shifts are $\nu_A = 30.0$ Hz, $\nu_B = 70.0$ Hz, coupling constant $J_{AB} = 10.0$ Hz and the delay time $\tau = 0.025$ sec. The nonequilibrium spin system is assumed to relax by the intramolecular dipolar interaction with the relaxation rate $r^D = 1.0$ Hz. The absolute mode of spectrum $S_{absolute}$ in Eq. (59) is selected.

90° pulse are distributed by the second pulse over all p-quantum coherences. The third 90° observng pulse brings the p-quantum coherences back to the direct observable single quantum coherences[22]. Wokaun and coworkers[23] had used this pulse sequence to excite the zero, single and double quantum signals of an AB system and shown how these can be utilized to sudy the interactions between the system and their surroundings. They simply measured the line widths of the related signals, from which the relaxation rate '$1/T_2$' could be extracted for each signals. The disadvantage of this pulse sequnce is the fact that the intensities of p-quantum signals depend on the setting of the transmitter frequency (offset frequency). A 180° echo pulse with the same phase (Figure 2(b)) between two 90° pulses eliminates this drawback, however one observes in this case only the single and double quantum coherences. The intensities of single and double quantum signals from this pulse sequence are mainly proportional to $\cos(\pi J_{AB}\tau)$ and $\sin(\pi J_{AB}\tau)$ respectively[22] and therefore the optimal condition for a simultaneous excitation of the single and double quantum coherences is given by $\cos(\pi J_{AB}\tau) = \sin(\pi J_{AB}\tau)$, $\tau = 1/(4J_{AB})$. A simulation of this pulse experiment using $\tau = 0.25$ sec is shown in Figure 3, represented in the absolute mode $S_{absolute}$ in Eq. (59), where the system is assumed to relax by the dipolar interaction. In this case the relaxation informations are concentrated in the line widths of the signals. The line width, however, is known to be a rather insenistive carrier of dynamic informations, because this can be also broadend by other factors such as field inhomogeneity.

To observe the relaxation effects in the more sensitive *line intensities* besides the line width, we introduce here a slightly modified pulse sequence. An additional delay time τ^* immediately after the generation of p-quantum coherences and before the t_1 evolution (Figure 2(c)) will let the individual coherences relax characteristically in relation to the interaction types. The variation of this *relaxation differentiating delay* τ^* enables to visualize the relaxation mechanisms in the coherence intensities rather than the insensitive line width in the 2 D spectrum. In Figure 4, the typical dissipation

Figure 4. The f_1 projections of multiquantum $2D$ spectra simulated using the the pulse sequence in Figure 2(c). The static parameters and the delay time τ are same as in Figure 3. The system relaxes (a) by the intramolecular dipolar interaction with $r^D = 1.0$ Hz and (b) by the randomly fluctuating fields around the nuclear sites with $r^R = 1.0$ Hz and $\varepsilon_{mm'} = 1.0$.

patterns of the single and double quantum coherences are compared with the variation of the delay τ^*. The double quantum coherence relaxes slower than the single quantum signals by the dipolar interation (Figure 4(a)), whereas in the case of the random field interaction the reversed relation can be observed (Figure 4(b)).

Conclusions

The increasing number of relaxation studies tends to avoid the use of simple notation 'T_1' or 'T_2', expressed in Bloch's equation. In fact, the complex phenomena of relaxation cannot be interpreted as the part by 'longitudinal' or 'transversal' time constant of each single signal independently. In this study a complete master equation has been formulated including the explicit form of relaxation superoperator, which describes the relaxation in relation to the molecular dynamics. The master operator contains besides the liouvillian for system of interest two interaction mechanisms, intramolecular dipolar and random external field interaction, which are mainly responsible for spin relaxation in solution NMR spectroscopy. The diagonal elements of the relaxation matrix express the relaxation behavior of the coherences, while the offdiagonal elements contain the information about the relation to each other. It has also been shown that the spectral densities can be compressed to the corresponding *relaxation rates*. The master and pulse operator formulated can trance the exact time history of the system during a multipulse experiment and therefore the whole dynamic informations inherent in the spin system are contained in the density vector and master operator. The FID in the detection period can *algebraically* reduced to the density vector and master and thus finally Fourier transformed *analytically* to frequency spectrum. The nonstationary spectrum can than be expressed by an intensity-determining *shape vector*, a frequency-determining *spectral vector* and a coherence-selecting projection operator. The algorithm, transferred to a simulation program CANDYS, will offer a more convinient way to study dynamic phenomena in general and tools to design special pulse sequence demanded for experimental works. Simulations in Figure 4 have shown how the maximum amount of relaxation information can be extracted using a modified $90°-180°-90°$ pulse sequence.

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