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NMR 吸收線 모양과 誘導磁氣自由減衰曲線 研究에의 投影演算子法의 應用

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Application of the Projection Operator Technique to the Study of NMR Line Shape and Free Induction Decay Curve

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要 約. 이 論文에서는 NMR 吸收線과 FID 曲線의 모양을 硏究함에 있어서의 projection operator 의 應用法을 探索하였다. 이 projection operator 法은 NMR 吸收線과 FID 函數를 硏究하는데에 基礎가 되는 한 벌의 hierarchy equation들을 誘導하는데에 便利한 手段이 됨을 밝혔다. 逐次近似法이나 적당한 decoupling 近似를 쓰면 이들 方程式은 NMR 吸收線이나 FID 函數를 理論的으로 計算하는데에 좋은 出發點이 될 수 있을 것이다. NMR 吸收線에 對한 간단한 linear response theory의 考察과 吸收線과 FID 函數間의 關係도 記述하였다.

ABSTRACT. In this paper application of the projection operator technique to the study of NMR absorption line shape and free induction decay curve is explored. It is found that the projection operator technique can provide a convenient means for deriving a set of hierarchy equations which may serve as a good starting point for theoretical calculation of the absorption line and free induction decay function by successive approximation or by an appropriate decoupling approximation. A brief review of linear response theory of NMR line shape and the relation between the absorption line shape and free induction decay function are also described.

1. INTRODUCTION

One of the basic problems in the theory of magnetic resonance is theoretical prediction of the resonance line and free induction decay shape in a paramagnetic spin system. Van Vleck[1] has shown that the resonance line shape can be expressed in terms of moments of the absorption line. However, in reality, mathematical complications prevent us from going beyond the calculation of the second and fourth moment.

Lowe and Norberg[2] have demonstrated that the free induction decay curve (hereafter, referred to as the FID curve) is equivalent to the Fourier transform of the absorption line if certain conditions are met and have proposed a theory to calculate the shape of FID curve. Their theory is based on the time expansion of FID function $\Phi(t)$ in the form

$$\Phi(t)=\sum_{n=0}^{\infty}\frac{t^n}{n!}F_n(t) \qquad (1)$$

where $F_n(t)$ is a certain function of time t whose explicit form is given in the original paper of Lowe and Norberg. The above expansion has actually been obtained by splitting the dipolar Hamiltonian into two parts, the Ising and exchange part. The Lowe-Norberg theory[2] was successful to describe the beats observed experimentally for solid CaF_2. But in this case, too, mathematical difficulty does not give us any possibiliy to go beyond the fourth-order term. Since the neglect of higher order terms in the expansion of $\Phi(t)$ with respect to t is not justified, it is also difficult to develop an entire theory along this line. Clough and McDonald[3] reexamined the Lowe-Norberg calculation and have shown that the series expansion (1) diverges for large t and tried to curb this difficulty without much success.

In the meantime Evans and Powles,[4] using a Dyson-type expansion, have also obtained a reasonable agreement with experimental results for short t. They have claimed that since it was not a power series expansion of t it could be used for large t. Unfortunately, in their theory it is also difficult to evaluate beyond the first two terms and the convergence of the series used has never been confirmed. Development of the theory along other lines also followed. Tjon[5], who also split the dipolar Hamiltonian into the exchange and Ising part, has proposed a theory based on quantum statistical mechanics. By introducing the so-called linearity assumption he has shown that $\Phi(t)$ satisfies the following integro-differential equation:

$$\frac{d}{dt}\Phi(t)=\int_0^t K(t-t')\Phi(t')dt' \qquad (2)$$

where the kernel $K(t)$ may be expressed as an infinite power series of t.

On the other hand Mansfield[6], adopting the method of Green's function developed in the quantum field theory, has also arrived at the same equation as Eq. (2). Yet Borckmans and Walgraef[7], using the theory for the Heisenberg spin system developed by Résibois and De Leener[8], have proposed another theory the result of which is represented by an equation similar to that obtained by Tjon.

In the theories developed by Tjon[5], Mansfield[6], and Borckmans and Walgraef[7], however, calculation of the kernel function $K(t)$ remains a formidable problem. Thus, in actual application of their theories they have been forced to assume a specific form of $K(t)$. In this paper we shall demonstrate that the projection operator method originally devised out by Zwanzig[9] and used for the study of infrared and optical absorption line shape in solids by Wilson, King, and Kim[10] and Greer and Rice[11] can be used to derive Eq. (2) in a much simpler manner. Moreover, this method enables us to derive a set of hierarchy equations which is basic to the study of kernel function $K(t)$. In fact a similar projection operator method has been adopted by Wang and Ramshaw[12] to explain the experimentally observed spin echo train in a multiple pulse experiment in dipolar solids. Unfortunately, however, their attention has been restricted to the study of echo train as a function of pulse interval and has not been extended to a more general problem like the NMR line and FID shape. Furthermore, the projection operator adopted by Wang and Ramshaw is of much simpler form compared to the one used in this paper. Such a simpler form of the projection operator cannot lead us to a set of hierarchy equations of $K(t)$.

It goes without saying that the study of FID function can give us important informations regarding the spin energy diffusion process occurring in dipolar solids. Recent development of the pulsed Fourier transform NMR spectroscopy has put further importance on exploring a systematic way of studying the line shape and FID function. Before delving into further detail of the problem the linear response theory of resonance line shape shall be briefly reviewed.

2. LINEAR RESPONSE THEORY OF MAGNETIC RESONANCE ABSORPTION LINE SHAPE

Suppose a quantum mechanical system described by a time-independent Hamiltonian $\mathscr{H}$ is perturbed by an external perturbation $\mathscr{H}'(t)$. If the system under consideration is a paramagnetic spin system as in the case of NMR experiments, then the perturbation $\mathscr{H}'(t)$ represents the interaction between the r. f. field and spin system.

In order to avoid transient effects occurring when the perturbation is first switched on we assume that the perturbation $\mathscr{H}'(t)$ is adiabatically turned on, that is, $\mathscr{H}'(-\infty)=0$. After the perturbation is turned on, the system evolves according to the following equation of motion for the density operator:[13]

$$\frac{\partial}{\partial t}\rho(t)=-\frac{i}{\hbar}[\mathscr{H}+\mathscr{H}'(t),\ \rho(t)] \qquad (3)$$

with the initial condition

$\rho(-\infty)=\rho_e$ (density operator for equilibrium ensemble)

$$=\frac{\exp(-\mathscr{H}/kT)}{\mathrm{Tr}\{\exp(-\mathscr{H}/kT)\}} \qquad (4)$$

where k is the Boltzmann constant and T the absolute temperature of the system.

In the interaction representation Eq. (3) may be rewritten in the following form:[14]

$$\frac{\partial}{\partial t}\tilde{\rho}(t)=-\frac{i}{\hbar}[\tilde{\mathscr{H}}'(t),\ \tilde{\rho}(t)] \qquad (5)$$

where

$$\tilde{\rho}(t)=e^{i\mathscr{H}t/\hbar}\ \rho(t)\ e^{-i\mathscr{H}t/\hbar} \qquad (6)$$

and

$$\tilde{\mathscr{H}}'(t)=e^{i\mathscr{H}t/\hbar}\ \mathscr{H}'(t)\ e^{-i\mathscr{H}t/\hbar} \qquad (7)$$

In the linear response scheme the solution of Eq. (5) is approximated by

$$\tilde{\rho}(t)\approx\rho_e-\frac{i}{\hbar}\int_{-\infty}^{t}[\tilde{\mathscr{H}}'(t'),\ \rho_e]dt'. \qquad (8)$$

Suppose now a system consisting of N nuclear spins of the same species is subjected to a linearly oscillating magnetic field $H_1(t)$ applied along the x-axis in the laboratory-fixed coordinates. Then $\mathscr{H}'(t)$ may be written in the following form:

$$\mathscr{H}'(t)=-\gamma\hbar I_x H_1(t), \qquad (9)$$

where I_x is the x-component of total spin angular momentum $\boldsymbol{I}$ defined by

$$\boldsymbol{I}=\sum_j \boldsymbol{I}_j \qquad (10)$$

with $\boldsymbol{I}_j$ denoting the spin angular momentum for the j-th spin in the system and γ represents the magnetogyric ratio for the given nuclear species.

Magnetization vector for the given spin system may now be defined by

$$\overrightarrow{\mathscr{M}}=\gamma\hbar\boldsymbol{I}/V \qquad (11)$$

where V is the volume of the spin system under consideration. Thus the statistical average of the x-component of $\overrightarrow{\mathscr{M}}$ at time t, $M_x(t)$, can be given by

$$M_x(t) = \mathrm{Tr}(\rho(t)\mathcal{M}_x) = \frac{1}{V}\gamma\hbar\ \mathrm{Tr}\{\tilde{\rho}(t)\tilde{I}_x(t)\} \tag{12}$$

where

$$\tilde{I}_x(t) = e^{i\mathscr{H}t/\hbar}\ I_x\ e^{-i\mathscr{H}t/\hbar} \tag{13}$$

and $\tilde{\rho}(t)$ has been previously defined by Eq. (6).

Substitution of Eqs. (7), (8) and (9) into Eq. (12) and a little manipulation can lead us to the expression

$$M_x(t) = \int_0^\infty \chi(\tau)\ H_1(t-\tau)d\tau \tag{14}$$

where the response function $\chi(\tau)$ is defined by

$$\chi(\tau) = \frac{i\gamma^2\hbar}{V}\langle[\tilde{I}_x(\tau),\ \tilde{I}_x(0)]\rangle. \tag{15}$$

The angular bracket notation in Eq. (15) represents the equilibrium ensemble average.

From Eq. (15) it can be seen that $\chi(\tau)$ is an odd real function of τ, that is,

$$\chi(-\tau) = -\chi(\tau) \text{ and } \chi^*(\tau) = \chi(\tau) \tag{16}$$

Let us Fourier-analyze $M_x(t)$ and $H_1(t)$ as follows.

$$M_x(t) = \int_{-\infty}^\infty M_x(\omega)\ e^{i\omega t}\ d\omega \tag{17}$$

and

$$H_1(t) = \int_{-\infty}^\infty H_1(\omega)\ e^{i\omega t}\ d\omega. \tag{18}$$

We also introduce the function $\chi(\omega)$ defined by

$$\chi(\omega) = \int_0^\infty \chi(t)\ e^{-i\omega t}\ dt. \tag{19}$$

Then, it follows from Eqs. (14), (17), (18) and (19) that

$$M_x(\omega) = \chi(\omega)\ H_1(\omega). \tag{20}$$

It is obvious from Eq. (20) that $\chi(\omega)$ is the magnetic susceptibility of the spin system. Also, Eqs. (16) and (19) tell us that

$$\chi^*(\omega) = \chi(-\omega). \tag{21}$$

Suppose now a magnetic field linearly oscillating with a particular frequency ω is applied to the spin system. Such a magnetic field can be expressed by

$$H_1(t) = H_1(e^{i\omega t} + e^{-i\omega t}). \tag{22}$$

In this case the average power absorbed by the spin system over one cycle of oscillation is given by

$$\begin{aligned}\mathcal{P} &= \frac{\omega}{2\pi}\int_0^{2\pi/\omega} H_1(t)[dM_x(t)/dt]dt \\ &= -2H_1^2\omega\,\mathcal{I}m[\chi(\omega)].\end{aligned} \tag{23}$$

On the other hand the time-dependent perturbation theory predicts that the total energy absorbed by the spin system per unit time is equal to[15]

$$\mathcal{P} = \pi H^2{}_1\omega\omega_0\chi_0 f(\omega) \tag{24}$$

where the function $f(\omega)$ represents the shape of magnetic resonance absorption line and χ_0 and ω_0 are, respectively, the static magnetic susceptibility and Larmor frequency for the given spin system.

Comparing Eq. (23) with Eq. (24), we obtain

$$f(\omega) = -\frac{2}{\pi\chi_0}\frac{1}{\omega_0}\mathcal{I}m[\chi(\omega)]. \tag{25}$$

Since the resonance absorption always occurs near $\omega=\omega_0$, to a good approximation ω_0 in Eq. (25) can be replaced by ω. Thus we have

$$f(\omega) = -\frac{2}{\pi\chi_0}\frac{1}{\omega}\mathcal{I}m\ [\chi(\omega)]. \tag{26}$$

Then, from Eqs. (15), (19), (21) and (26) we can obtain the following expression for $f(\omega)$:

$$f(\omega) = -\frac{\gamma^2\hbar}{\pi V\chi_0}\frac{1}{\omega} \times\int_{-\infty}^\infty \langle[\tilde{I}_x(t),\ \tilde{I}_x(0)]\rangle\ e^{-i\omega t}dt. \tag{27}$$

Consider now the integral appearing in Eq. (27). By making use of the relation (see the Appendix)

$$\int_{-\infty}^\infty \langle\tilde{I}_x(t)\tilde{I}_x(0)\rangle\ e^{-i\omega t}dt = e^{-\hbar\omega/kT}\int_{-\infty}^\infty \langle\tilde{I}_x(0)\tilde{I}_x(t)\rangle e^{-i\omega t}\ dt \tag{28}$$

the above integral may be rewritten as

$$\int_{-\infty}^{\infty} \langle [\tilde{I}_x(t),\ \tilde{I}_x(0)] \rangle\ e^{-i\omega t}dt$$
$$=(1-e^{\hbar\omega/kT})\int_{-\infty}^{\infty} \langle \tilde{I}_x(\mathrm{t})\tilde{I}_x(0)\rangle e^{-i\omega t}dt. \qquad (29)$$

Since $\hbar\omega$ is much smaller than kT under conditions of NMR experiments, $e^{\hbar\omega/kT}$ and ρ_e can, respectively, be approximated by $1+\hbar\omega/kT$ and $(\mathrm{Tr}\ e^{-\mathscr{H}/kT})^{-1}$. Thus from Eqs. (27) and (29) we obtain

$$f(\omega)=\frac{\gamma^2\hbar^2}{V\pi\chi_0}\ \frac{1}{ZkT}$$
$$\times\int_{-\infty}^{\infty} \mathrm{Tr}\{\tilde{I}_x(t)\tilde{I}_x(0)\}e^{-i\omega t}dt, \qquad (30)$$

where we have used the notation Z to denote the partition function $\mathrm{Tr}(e^{-\mathscr{H}/kT})$.

At this stage it will be convenient to split the spin Hamiltonian $\mathscr{H}$ into two parts, the Zeeman term $\mathscr{H}_0$ and the remaining part $\mathscr{H}_1$, that is,

$$\mathscr{H}=\mathscr{H}_0+\mathscr{H}_1, \qquad (31)$$

where $\mathscr{H}_0$ can be explicitly written as

$$\mathscr{H}_0=-\hbar\omega_0 I_z. \qquad (32)$$

Abragam[16] has shown that in studying the magnetic resonance line shape we have only to pay our attention to the case in which $\mathscr{H}_0$ and $\mathscr{H}_1$ commute with each other. Thus, hereafter, it is assumed that $\mathscr{H}_0$ and $\mathscr{H}_1$ commute with each other. Then the operator $\tilde{I}_x(t)$ can be explicitly rewritten as

$$\tilde{I}_x(t)=e^{i\mathscr{H}_1 t/\hbar}\ e^{-i\omega_0 I_z t}I_x\ e^{i\omega_0 I_z t}\ e^{-i\mathscr{H}_1 t/\hbar} \quad (33)$$

Now consider a new coordinate system rotating about the z-axis of the laboratory-fixed coordinate system with the angular velocity ω_0, as shown in *Fig.* 1. Let us denote this coordinate system by $(X,\ Y,\ Z)$ in contrast to the laboratory-fixed coordinates $(x,\ y,\ z)$. The z- and Z-axis always coincide with each other. Suppose at $t=0$ two coordinate systems completely coincide with each other. Then it can be shown that[17]

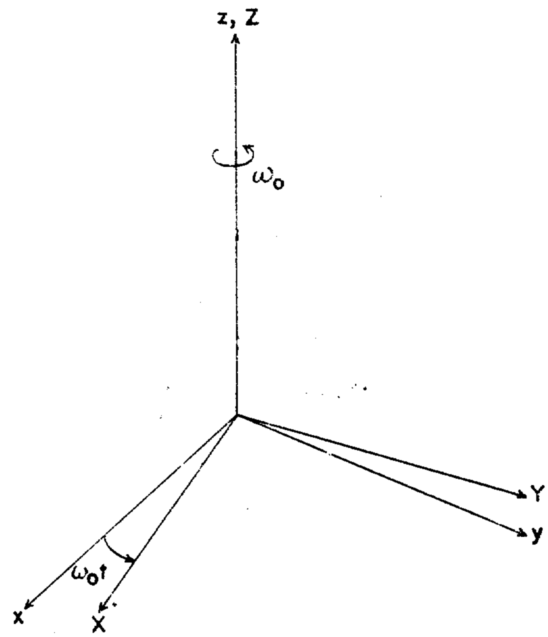

Fig. 1 Rotating coordinates.

$$e^{-i\omega_0 I_z t}I_x e^{i\omega_0 I_z t}=I_X \qquad (34)$$

where I_X is the X-component of $\boldsymbol{I}$ in the rotating frame. Let us introduce the operator $I_X^*(\mathrm{t})$defined by

$$I_X^*(t)=e^{i\mathscr{H}_1 t/\hbar}I_X e^{-i\mathscr{H}_1 t/\hbar} \qquad (35)$$

Then Eq. (30) may be rewritten as

$$f(\omega)=\frac{\gamma^2\hbar^2}{V\pi\chi_0}\ \frac{1}{ZkT}$$
$$\times\int_{-\infty}^{\infty} Tr\{I_X^*(t)I_X^*(0)\}e^{-i\omega t}\ dt \qquad (36)$$

As shall be shown in the next section, the term $\mathrm{Tr}\{I_X^*(t)I_X^*(0)\}$ represents the FID function obtained in a single pulse experiment. Therefore, apart from the constant factors in Eq. (36), we may say that the resonance absorption line is equivalent to the Fourier transform of FID function.

3. FREE INDUCTION DECAY IN A SINGLE PULSE EXPERIMENT

A nuclear spin system at thermal equilibrium in the presence of a strong static magnetic field can, to a good approximation, be described by the equilibrium density operator

$$\rho_e \cong Z^{-1} e^{-\mathcal{H}_0/kT}$$
$$\cong Z^{-1}\left(1+\frac{\hbar\omega_0}{kT} I_z\right). \quad (37)$$

Suppose we now apply a short, intense 90° pulse along the y-axis to the spin system at $t=0$. Then, immediately after the pulse is cut off, $\rho(t)$ takes the form

$$\rho(0) = e^{-i(\pi/2)I_y} \rho_e \; e^{i(\pi/2)I_y}$$
$$= Z^{-1}\left(1+\frac{\hbar\omega_0}{kT} I_x\right). \quad (38)$$

After the pulse is turned off, the density operator for the system evolves according to the equation

$$\frac{\partial}{\partial}\boldsymbol{\rho}(t) = -\frac{i}{\hbar}\left[\mathcal{H}_0+\mathcal{H}_1,\ \rho(t)\right], \quad (39)$$

the formal solution of which can be written as

$$\rho(t) = e^{-i(\mathcal{H}_0+\mathcal{H}_1)t/\hbar}\rho(0)e^{i(\mathcal{H}_0+\mathcal{H}_1)t/\hbar}$$
$$= Z^{-1}\left(1+\frac{\hbar\omega_0}{kT} e^{i\omega_0 I_z t} e^{-i\mathcal{H}_1 t/\hbar} I_x e^{-i\omega_0 I_z t} e^{i\mathcal{H}_1 t/\hbar}\right) \quad (40)$$

Since the amplitude of FID signal is proportional to the instantaneous magnitude of the x-component of magnetization vector, we may write apart from the proportionality constant

$$\Phi(t) = \mathrm{Tr}\{\rho(t) I_x\} \quad (41)$$

Substituting Eq. (40) into Eq. (41) and using Eqs. (34) and (35), we may obtain

$$\Phi(t) \propto \mathrm{Tr}\{I_X^*(t)\ I_X^*(0)\}. \quad (42)$$

Thus we have seen that $\mathrm{Tr}\{I_X^*(t) I_X^*(0)\}$ describes the FID function in a single pulse experiment.

4. APPLICATION OF THE PROJECTION OPERATOR TECHIQUE TO THE STUDY OF NMR LINE SHAPE AND FREE INDUCTION DECAY

From the definition of $I_X^*(t)$ [see Eq. (35)] we can see that its time evolution is governed by the equation

$$\frac{\partial}{\partial t} I_X^*(t) = i\mathcal{L}\, I_X^*(t) \quad (43)$$

where the Liouville-type operator $\mathcal{L}$ is defined by

$$\mathcal{L} = \hbar^{-1}[\mathcal{H}_1,\ ]. \quad (44)$$

Consecutive operations of $\mathcal{L}$ thus have the meaning

$$\mathcal{L}^n\hat{O} = \hbar^{-n}\underbrace{[\mathcal{H}_1, [\mathcal{H}_1, \cdots\cdots[\mathcal{H}_1,}_{n \text{ times}}\ \hat{O}]]\cdots\cdots] \quad (45)$$

for any operator $\hat{O}$.

The formal solution of Eq. (43) may be written in the following form:

$$I_X^*(t) = e^{i\mathcal{L}t} I_X^*(0). \quad (46)$$

Comparing Eq. (46) with Eq. (35), we see that the operator $e^{i\mathcal{L}t}$ is formally equal to the sandwich operator $e^{i\mathcal{H}_1 t/\hbar}(\quad)e^{-i\mathcal{H}_1 t/\hbar}$, that is,

$$I_X^*(t) = e^{i\mathcal{L}t} I_X^*(0)$$
$$= e^{i\mathcal{H}_1 t/\hbar}\ I_X^*(0) e^{-i\mathcal{H}_1 t/\hbar} \quad (47)$$

We now introduce a set of operators P_n's and functions $f_n(t)$'s defined by

$$P_n\,\hat{O} = \frac{\mathrm{Tr}[(\mathcal{L}^n I_X^*)\hat{O}]}{\mathrm{Tr}[(\mathcal{L}^n I_X^*)^2]}\ \mathcal{L}^n I_X^* \quad (48)$$

and

$$f_n(t) = \frac{\mathrm{Tr}[(\mathcal{L}^n I_X^*) e^{i\mathcal{L}t} (\mathcal{L}^n I_X^*)]}{\mathrm{Tr}[(\mathcal{L}^n I_X^*)^2]} \quad (49)$$

In the above definitions we have used the abbreviated notation I_X^* for $I_X^*(0)$. We can immediately notice that $f_0(t)$ is proportional to our FID function $\Phi(t)$. In fact $f_0(t)$ is the normalized form of $\Phi(t)$.

From the definition of P_n's we see that they are linear operators and commute with time derivative operator $\partial/\partial t$. Moreover, they are idempotent, that is, $P_n^2 = P_n$. Therefore the operators P_n's are the so-called projection operators.

Consider now an operator $O_n(t)$ defined by

$$O_n(t)=e^{i\mathscr{L}t}(\mathscr{L}^n I_X^*). \tag{50}$$

From the definition of P_n's it is easy to confirm that the following relations hold:

$$\begin{aligned} &P_n O_n(0)=O_n(0)\\ &(1-P_n)O_n(0)=0\\ &P_n O_n(t)=\mathscr{L}^n I_X^* f_n(t)\\ &P_n\left\{\frac{\partial}{\partial t}O_n(t)\right\}=\mathscr{L}^n I_X^*\frac{d}{dt}f_n(t), \end{aligned} \tag{51}$$

etc.

For convenience we will from now on drop the time symbol from all the operators whenever we refer to $t=0$.

Since for any operator $O(t)$ we may write

$$O(t)=P_nO(t)+(1-P_n)O(t), \tag{52}$$

we have from the definition of $O_n(t)$

$$\begin{aligned} P_n[(\partial/\partial t)O_n(t)]&=iP_n\mathscr{L}O_n(t)\\ &=i\ P_n\mathscr{L}P_nO_n(t)+i\ P_n\mathscr{L}(1-P_n)O_n(t) \end{aligned} \tag{53}$$

and

$$\begin{aligned} (1-P_n)\ [(\partial/\partial t)O_n(t)]&=i(1-P_n)\mathscr{L}O_n(t)\\ &=i(1-P_n)\mathscr{L}P_nO_n(t)\\ &\quad+i(1-P_n)\mathscr{L}(1-P_n)O_n(t). \end{aligned} \tag{54}$$

Integration of Eq. (54) with respect to time t yields

$$\begin{aligned} &(1-P_n)O_n(t)\\ &=i\int_0^t dt'\exp[i(1-P_n)\mathscr{L}(t-t')]\\ &\quad(1-P_n)\mathscr{L}P_nO_n(t'), \end{aligned} \tag{55}$$

where we have taken into account the fact that

$$(1-P_n)O_n=0.$$

Substitution of Eq. (55) into (53) and a little manipulation gives us

$$\frac{d}{dt}f_n(t)=\int_0^t K_n(t-t')f_n(t')dt' \tag{56}$$

where

$$K_n(t)=\frac{\mathrm{Tr}\{(\mathscr{L}^{n+1}I_X^*)\exp[i(1-P_n)\mathscr{L}t](1-P_n)\mathscr{L}^{n+1}I_X^*\}}{\mathrm{Tr}\{(\mathscr{L}^nI_X)^2\}} \tag{57}$$

In deriving Eqs. (56) and (57) use has been made of the fact that

$$\mathrm{Tr}(A\mathscr{L}B)=-\mathrm{Tr}\{(\mathscr{L}A)B\} \tag{58}$$

and

$$\mathrm{Tr}\{(\mathscr{L}^mI_X^*)(\mathscr{L}^n{}_X{}^*I)\}=0\ \text{for}\ m+n=\text{odd}. \tag{59}$$

Eq. (56) tells us that the spin energy diffusion processes are in general governed by a non-Markoffian equation. In case $n=0$ Eq. (56) reduces to the equation first derived by Tjon[5] for dipolar solids who has split the dipolar Hamiltonian into the Ising and exchange part. However, it is clear from our derivation of Eq. (56) that split of the dipolar Hamiltonian into two parts is merely for convenience and is of no absolute necessity.

In order to derive a set of hierarchy equations of $K_n(t)$ let us now consider the operator

$$\hat{A}_n(t)=\exp[i(1-P_n)\mathscr{L}t](1-P_n)\mathscr{L}^{n+1}I_X^*. \tag{60}$$

The time derivative of $\hat{A}_n(t)$ may be written as

$$\begin{aligned} \partial/\partial t\ \hat{A}_n(t)&=i(1-P_n)\mathscr{L}\ \hat{A}_n(t)\\ &=i\mathscr{L}\hat{A}_n(t)-i\ P_n\ \mathscr{L}\ \hat{A}_n(t) \end{aligned} \tag{61}$$

Since $P_n\mathscr{L}\hat{A}_n(t)=-\mathscr{L}^nI_X^*K_n(t)$, we have from Eq. (61)

$$\frac{\partial}{\partial t}\hat{A}_n(t)=i\mathscr{L}\hat{A}_n(t)+i\mathscr{L}^nI_X^*K_n(t) \tag{62}$$

By operating P_{n+1} and $1-P_{n+1}$ on both sides of Eq. (62) we have

$$\begin{aligned} \frac{\partial}{\partial t}P_{n+1}\hat{A}_n(t)&=iP_{n+1}\mathscr{L}P_{n+1}\hat{A}_n(t)\\ &\quad+iP_{n+1}\ \mathscr{L}(1-P_{n+1})\hat{A}_n(t) \end{aligned} \tag{63}$$

and

$$\begin{aligned} \frac{\partial}{\partial t}(1-P_{n+1})\hat{A}_n(t)&=i(1-P_{n+1})\mathscr{L}P_{n+1}\hat{A}_n(t)\\ &\quad+i(1-P_{n+1})\mathscr{L}(1-P_{n+1})\hat{A}_n(t)\\ &\quad+i\mathscr{L}^nI_X^*K_n(t), \end{aligned} \tag{64}$$

where we have used the relations $P_{n+1}\ \mathscr{L}^nI_X^*=0$ and $(1-P_{n+1})\ \mathscr{L}^nI_X^*=\mathscr{L}^nI_X^*$.

Integration of Eq. (64) with respect to time yields

$$(1-P_{n+1})\hat{A}_n(t) = i\frac{1}{D_{n,n+1}}\int_0^t dt' e^{i(1-P_{n+1})\mathcal{L}(t-t')} \mathcal{L}^{n+2} I_X^* K_n(t') + i\int_0^t dt' e^{i(1-P_{n+1})\mathcal{L}(t-t')} \mathcal{L}^n I_X^* K_n(t'), \tag{65}$$

where

$$D_{n,n+1} = \frac{Tr\{(\mathcal{L}^{n+1}I_X^*)^2\}}{Tr\{(\mathcal{L}^n I_X^*)^2\}} \tag{66}$$

Substitution of Eq. (65) into Eq. (63) produces

$$\frac{d}{dt}K_n(t) = -D_{n,n+1}\int_0^t K_n(t')dt' + \int_0^t K_{n+1}(t-t')K_n(t')dt', \tag{67}$$

which is a set of hierarchy equations of $K_n(t)$'s.

In order to treat coupled equations such as Eq. (67) more elegantly we now introduce the half-interval Fourier transform defined by

$$\tilde{F}(\omega) = \lim_{\eta\to 0^+}\int_0^\infty F(t)e^{-i\omega t-\eta t}\, dt, \tag{68}$$

where the factor $e^{-\eta t}$ has been inserted to guarantee the convergence of defined integral.

Taking the half-interval Fourier transform of Eq. (56) and Eq. (67), we have

$$\tilde{f}_n(\omega) = \lim_{\eta\to 0^+}\frac{1}{i\omega+\eta-\tilde{K}_n(\omega)} \tag{69}$$

and

$$\tilde{K}_n(\omega) = \lim_{\eta\to 0^+}\frac{D_{n,n+1}}{i\omega+\eta+\dfrac{D_{n,n+1}}{i\omega+\eta}-\tilde{K}_{n+1}(\omega)} \tag{70}$$

In particular, for $n=0$ we may write

$$f_0(\omega) = \lim_{\eta\to 0^+}\frac{1}{i\omega+\eta-\tilde{K}_0(\omega)} \tag{71}$$

and

$$\tilde{K}_0(\omega) = \lim_{\eta\to 0^+}\frac{D_{0,1}}{i\omega+\eta+\dfrac{D_{0,1}}{i\omega+\eta}-\tilde{K}_1(\omega)}, \tag{72}$$

of which the second equation may be rewritten in the form of an infinite continued fraction as follows:

$$\tilde{K}_0(\omega) = \lim_{\eta\to 0^+} \cfrac{D_{0,1}}{i\omega+\eta+\cfrac{D_{0,1}}{i\omega+\eta}-\cfrac{D_{1,2}}{i\omega+\eta+\cfrac{D_{1,2}}{i\omega+\eta}-\cfrac{D_{2,3}}{i\omega+\eta+\cdots}}} \tag{73}$$

Such an infinite continued fractional form may provide us a convenient means of studying the resonance line shape with the aid of modern computers.

Earlier investigators[5,6] have been forced to assume a specific form of $K_0(t)$ because they could not derive a set of coupled equations such as Eq. (67). In our case, however, due to the presence of Eq. (67) such an assumption can be introduced at as high a stage as we want. Moreover, the convergence problems with respect to time t never arise because $K_0(t)$ is obtained through the solution of integro-differential equation such as Eq. (67), not by expanding into the power series of time t.

Even at this stage we can gain some informations about the resonance absorption line shape by looking at $\tilde{f}_0(\omega)$. Since $f_0(t)$ is an even real function of time t, we can see that

$$\int_{-\infty}^{\infty} f_0(t)e^{-i\omega t}\, dt = 2\,Re[\tilde{f}_0(\omega)], \tag{74}$$

whence the resonance line shape can be studied by lookinginto the real part of $\tilde{f}_0(\omega)$. Since from Eq. (71) we may write

$$Re[\tilde{f}_0(\omega)] = -\frac{Re[\tilde{K}_0(\omega)]}{\{\omega-\mathcal{I}m[\tilde{K}_0(\omega)]\}^2+\{Re[\tilde{K}_0(\omega)]\}^2}$$

the absorption line peaked about $\omega=\omega_0$ may be described by the following function:

$$Re[\tilde{f}_0(\omega-\omega_0)] = -\frac{Re[\tilde{K}_0(\omega-\omega_0)]}{\{\omega-\omega_0-\mathcal{I}m[\tilde{K}_0(\omega-\omega_0)]\}^2+\{Re[\tilde{K}_0(\omega-\omega_0)]\}^2}, \tag{75}$$

In case $\tilde{K}_0(\omega)$ is independent of ω, Eq. (75)

provides the well known Lorentzian line shape.

We have to remark here that the infinite continued fractional form of $\tilde{K}_0(\omega)$ given by Eq. (73) somewhat resembles a function used by Kubo[18] for stochastic study of the NMR line shape. However, in deriving Eq. (73) we have never used any stochastic assumptions and our equation (73) is strictly exact in this sense. We also would like to point out that the projection operator P_n reduces to that used by Wang and Ramshaw[12] in case $n=0$. Thus we may say that the method of Wang and Ramshaw is a special case of more general one described in this paper.

In order to apply the theory developed here to the study of NMR line shape and free induction decay for an actual spin system we need the knowledge of $\mathscr{H}_1$ which will differ for different systems. In our next paper we will apply the method developed here to make theoretical calculation of the FID curve in the solid CaF_2 attempted by earlier investigators.

5. CONCLUSION AND DISCUSSION

In this paper we have shown that the projection operator technique can provide a convenient means for derivation of a set of hierarchy equations which is basic to the study of NMR line shape and free induction decay. These coupled integro-differential equations are of non-Markoffian character and may be treated more elegantly by introducing the half-interval Fourier transform of $f_n(t)$ and $K_n(t)$. It is of no doubt that the same method as shown in this paper can be applied to the study of echo train obtained in multiple pulse experiment without much ado.

APPENDIX

Suppose $A(t)$ and $B(0)$ represent two arbitrary Heisenberg operators, respectively, for $t=t$ and $t=0$. From the definition of $\langle A(t)B(0)\rangle$ we may write

$$\int_{-\infty}^{\infty}\langle A(t)B(0)\rangle e^{-i\omega t}dt = \frac{1}{\mathrm{Tr}(e^{-\beta\mathscr{H}})}\int_{-\infty}^{\infty}\mathrm{Tr}\{A(t)B(0)e^{-\beta\mathscr{H}}\}e^{-i\omega t}dt, \tag{A-1}$$

where $\beta=1/kT$ with k being the Boltzmann constant and T the absolute temperature.

In the representation in which $\mathscr{H}$ is diagonal we may write

$$\int_{-\infty}^{\infty}\mathrm{Tr}\{A(t)B(0)e^{-\beta\mathscr{H}}\}e^{-i\omega t}dt = \sum_{m,n}\int_{-\infty}^{\infty}\langle m|A(t)|n\rangle\langle n|B(0)|m\rangle e^{-\beta E_m}e^{-i\omega t}dt, \tag{A-2}$$

where we have noted the quantum mechanical closure relation

$$\sum_n |n\rangle\langle n|=1 \tag{A-2}$$

and the fact that

$$e^{-\beta\mathscr{H}}|m\rangle=e^{-\beta E_m}|m\rangle. \tag{A-4}$$

Using the definition of a Heisenberg operator, $A(t)$, we obtain

$$\int_{-\infty}^{\infty}\mathrm{Tr}\{A(t)B(0)e^{-\beta\mathscr{H}}\}e^{-i\omega t}dt = \sum_{m,n}\langle m|A(0)|n\rangle\langle n|B(0)|m\rangle e^{-\beta E_m} \times\int_{-\infty}^{\infty}e^{-i\omega t-i(E_n-E_m)t/\hbar}\,dt. \tag{A-5}$$

From the definition of Dirac δ-function

$$\delta(x)=\frac{1}{2\pi}\int_{-\infty}^{\infty}e^{-ixy}\,dy \tag{A-6}$$

we see that the the integral in (A-5) makes all the terms in the summation vanish except those satisfying the relation

$$\omega=(E_m-E_n)/\hbar$$

or

$$E_m=E_n+\hbar\omega. \tag{A-7}$$

Substitution of (A-7) into (A-5) and interchange of the order of summation over dummy indices n and m lead to

$$\int_{-\infty}^{\infty} \mathrm{Tr}\{A(t)B(0)e^{-\beta\mathscr{H}}\}e^{-i\omega t}dt$$
$$=e^{-\beta\hbar\omega}\sum_{n,m}\int_{-\infty}^{\infty}\langle n|B(0)|m\rangle\langle m|A(t)|n\rangle$$
$$e^{-\beta E_m}e^{-i\omega t}dt$$
$$=e^{-\beta\hbar\omega}\int_{-\infty}^{\infty} \mathrm{Tr}\{B(0)A(t)e^{-\beta\mathscr{H}}\}e^{-i\omega t}\,dt, \quad \text{(A-8)}$$

which, when combined with (A-1), produces

$$\int_{-\infty}^{\infty} \langle A(t)B(0)\rangle e^{-i\omega t}dt$$
$$=e^{-\beta\hbar\omega}\int_{-\infty}^{\infty} \langle B(0)A(t)\rangle e^{-i\omega t}dt.$$

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