

COMPARISON BETWEEN THE KINETIC THEORY AND GENERALIZED
MASTER EQUATION DERIVATIONS OF GAS PHASE NUCLEAR
MAGNETIC RELAXATION*

by

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ABSTRACT

The formulation of nuclear magnetic relaxation of polyatomic gases via the kinetic theory approach is discussed with respect to its relationship to the Generalized Master Equation approach. Neither approaches are developed in this paper, nor is the binary gas expansion undertaken, since these are well known. Rather the approximations used in deriving the Redfield equation from both approaches are explicitly compared. In particular the rotating frame approximation is shown to be equivalent to a Markoffian and weak coupling approximation.

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I. INTRODUCTION

Nuclear magnetic relaxation has been described almost exclusively within the framework of linear response and time correlation function theory.^{1,2} For dilute gases, the kinetic theory approach has also been pursued over the last few years,³⁻⁹ and provides an alternative description to the time correlation approaches. The motivation for the kinetic theory approach lay in two areas. First the explicit way in which binary collisions were treated gives a clear and well established method by which correlation times can be evaluated and interpreted in terms of the intermolecular potential. Secondly, it made the connection between the cross sections which are available from other transport phenomena. Traditionally transport properties of gases are treated within a kinetic theory framework. Certainly the same goals are also attainable from the correlation function approach, although little attention has been given to the actual evaluation of the correlation times in NMR.¹⁰ Moreover the connection between the two approaches of formulating NMR has received scant attention.¹¹ The purpose of this paper is to establish this connection by studying the approximations used in both approaches.

The Generalized Master Equation (GME) method due to Zwanzig¹² and the subsequent application of the GME to spin systems has received a great deal of attention¹³⁻¹⁶ and will be quoted here freely. Moreover, the binary gas expansion of the GME has been studied¹⁷ for quantum systems. In fact it has been shown that the resolvent $(\omega - L^{(N)})^{-1}$ where $L^{(N)}$ is the N particle Liouville superoperator containing pair interaction only, can be written in terms of $M(\omega)$; a superoperator containing all the information about the molecular interactions. Averaging over the "bath" variables, $\langle M \rangle$, and

expanding $\langle M \rangle$ in powers of the gas density results in Fano's $\langle m(\omega) \rangle$ superoperator being the first-order term. It has been established¹⁰ that $\langle m(\omega) \rangle$ is equivalent to the generalized Boltzmann collision superoperator $-iR(\omega)$ which is valid for molecules with quantum mechanical internal states when ω is an eigenfrequency of the operator upon which it acts. (In fact the collision superoperator R picks out the spectral frequencies of the operator upon which it operates, so that $R(\omega)$ is one spectral component of R .) It is therefore not necessary to discuss in any depth the binary gas expansion, nor the equivalence of the collision terms. As a consequence, throughout this paper, one molecule density operators are used, and no connection to the N -particle system is made.

With the above discussion in mind, it may seem that the connection between the two formulations is already established. In theory this is true, but in practice it has not been clear how the approximation used in the two approaches compare, nor have the Redfield equations been presented from the kinetic theory approach. This paper aims at elucidating these aspects.

In section II, the moment equations are rewritten in operator form so that it is clear that taking moments effectively projects out the pure spin part of the density operator from the irrelevant lattice part. These equations are then solved using the rotating frame approximation which has been extensively used in the kinetic theory approach. The resulting equation for the spin part of the density operator are the Redfield equations for dilute gases in operator form. In section III it is shown how the rotating frame approximation can be derived by making use of two standard approximations in the GME approach; namely a Markoffian and weak coupling approximation. A third approximation required is that the

intramolecular coupling hamiltonian must be isotropic. In gases and liquids this is a valid approximation. Thus the rotating frame approximation is not merely a transformation to the interaction representation, although it may be advantageous to view the moment equations in a rotating frame.⁶ A discussion concludes the paper.

II. SOLUTION OF THE MOMENT EQUATIONS

The kinetic theory approach to deriving Nuclear Magnetic Relaxation starts with the linearized Boltzmann Equation, ($\hbar = 1$)

$$i \frac{\partial \phi}{\partial t} = L_{\text{int}} \phi - i R \phi . \quad (1)$$

Here ϕ is the linear deviation from the equilibrium density operator ρ_0 so that the one-molecule density operator is

$$\rho = \rho_0(1 + \tilde{\phi}) . \quad (2)$$

The tilde denotes the Kubo transform ($\beta^{-1} = kT$)

$$\tilde{A} \equiv \beta^{-1} \int_0^\beta e^{xH_{\text{int}}} A e^{-xH_{\text{int}}} dx \quad (3)$$

where H_{int} is the one-molecule internal state hamiltonian (no intermolecular potential). For nuclear spin relaxation of dilute gases this is written as,

$$H_{\text{int}} = H_{\text{ZI}} + H_{\text{L}} + H_{\text{C}} . \quad (4)$$

Here H_{ZI} is the nuclear Zeeman hamiltonian,

$$H_{\text{ZI}} = \omega_{\text{I}} I_{\text{Z}} . \quad (5)$$

H_{L} is the "lattice" hamiltonian comprised of the rotational Zeeman hamiltonian

$$H_{ZI} = \omega_I I_Z \quad (6)$$

and a rotational hamiltonian, H_{rot} ,

$$H_L = H_{ZJ} + H_{rot} \quad (7)$$

H_C denotes the spin-lattice coupling hamiltonian. For dilute gases, H_C may be a spin-rotation, dipolar or quadrupolar intramolecular hamiltonian.

It is also convenient to define the corresponding Liouville superoperator,

$$\begin{aligned} L_{int} &= L_{ZI} + L_{ZJ} + L_{rot} + L_C \\ &\equiv L_{ZI} + L_L + L_C \end{aligned} \quad (8)$$

where the notation is obvious. In particular the rotational and nuclear Zeeman Liouville superoperator are,

$$L_{ZI} = \omega_I I_Z ; \quad L_{ZJ} = \omega_J J_Z \quad (9)$$

defining the commutator relations,

$$I_Z A = [I_Z, A]_- ; \quad J_Z A = [J_Z, A]_- \quad (10)$$

The moment method in kinetic theory amounts to expanding ϕ in powers of all possible polarizations, and retaining only those terms which

hopefully account for the dominant processes. For example, since the nuclear magnetization is of interest, $M = -\gamma_T \langle \underline{I} \rangle$, it is necessary that part of ϕ be at least of the form^{18,19} $\underline{P} \cdot \underline{I}$ where \underline{P} is proportional to the nonequilibrium nuclear spin polarization and \underline{I} is the nuclear spin operator. Consequently, ϕ is written as

$$\phi = \phi^{\underline{I}} + \phi^{\underline{L}}. \quad (11)$$

Here $\phi^{\underline{I}}$ describes pure nuclear spin nonequilibrium polarizations and is

$$\phi^{\underline{I}} = \sum_{\alpha, \alpha'} |\alpha\rangle \phi_{\alpha\alpha'}^{\underline{I}} \langle \alpha'| \quad (12)$$

where $|\alpha\rangle$, $\langle \alpha'|$ denote nuclear spin states, $\phi^{\underline{L}}$ accounts for the remaining polarization which may influence $\phi^{\underline{I}}$. Such a separation can be accomplished by use of projection operators. However the same partitioning is effectively accomplished by finding the average value of the nuclear spin \underline{I} and some appropriate lattice observable χ ,

$$i \frac{\partial \langle \underline{I} \rangle}{\partial t} = \langle \langle \underline{I} | L_{\underline{I}} | \phi^{\underline{I}} \rangle \rangle + \langle \langle \underline{I} | L_{\underline{C}} | \phi^{\underline{L}} \rangle \rangle \quad (13)$$

$$i \frac{\partial \langle \chi \rangle}{\partial t} = \langle \langle \chi | (L_{\text{int}} - i R)^{-1} | \phi^{\underline{L}} \rangle \rangle + \langle \langle \chi | L_{\underline{C}} | \phi^{\underline{I}} \rangle \rangle. \quad (14)$$

The average value $\langle \rangle$ is just

$$\langle A \rangle = \langle A \rangle_{\text{eq}} + \text{tr} \rho_0 \hat{\phi} A \quad (15)$$

with

$$\langle A \rangle_{\text{eq}} = \text{tr } \rho_0 A. \quad (16)$$

The inner product is defined by

$$\langle\langle A|B \rangle\rangle = \text{tr}_{I,L} A^\dagger \rho_0 \bar{B}. \quad (17)$$

† is the ordinary operator adjoint and the trace is over both spin and lattice states.

By removing the trace over the spin variables in Eq. (13), and over spin and lattice variables in Eq. (14), operator equations are obtained for ϕ^I and ϕ^L ,

$$i \frac{\partial \phi^I}{\partial \tau} = L_{2I} \phi^I + \text{tr}_L L_C \rho_0 X \quad (18)$$

and

$$i \frac{\partial \phi^L}{\partial \tau} = (L_{\text{int}} - i R) \phi^L + L_C \phi^I. \quad (19)$$

The assumption that collisions are not effective at changing nuclear spins is built into Eq. (14) and (18), i.e. $R \phi^I = 0$.

In this form, Eqs. (18) and (19) are the type of equation expected from a projection operator technique. It is therefore possible to proceed via the method of deriving the equation of motion for ϕ^I by integrating Eq. (19) and substituting the result into Eq. (18). The result is a

non-Markoffian equation for ϕ^I valid for dilute gases. Rather than proceeding in that manner the rotating frame approximation is used, namely,

$$i \frac{\partial \phi^L}{\partial t} = \omega_I \hat{J}_Z \phi^L \quad (20)$$

and Eq. (19) is solved to give,

$$\phi^L = (L_{\text{int}} - \omega_I \hat{J}_Z - i R)^{-1} L_C \phi^I. \quad (21)$$

The frequency is just the nuclear Larmour precession frequency. The rotation operator \hat{J}_Z rotates all the states about the magnetic field direction,

$$\hat{J}_Z A = (J_Z + J_Z)A = [I_Z + J_Z, A]_-. \quad (22)$$

(Here it is assumed that all the degrees of freedom except the rotation and nuclear operators are isotropic.)

Substitution of Eq. (21) into Eq. (18) gives the Redfield equations for dilute gases in operator form,

$$i \frac{\partial \phi^I}{\partial t} = \omega_I I_Z \phi^I + \text{tr}_L L_C \rho_0 (L_{ZJ} + L_{\text{Rot}} - \omega_I \hat{J}_Z - i R)^{-1} L_C \phi^I. \quad (23)$$

The superoperator L_C has been neglected in the resolvent since this includes higher than second-order couplings between the spin and the lattice. For weak intramolecular coupling this is a good approximation.¹⁶

III. DERIVATION OF THE ROTATING FRAME APPROXIMATION

The usual procedure for obtaining Eq. (23), is to make a Markoffian approximation and allow the integration limit $t \rightarrow \infty$ after projecting out the relevant part of ρ with a projection operator P . The resulting equation for $P\rho$ is the same as Eq. (23) if the following identifications are made

$$P L P = L_I, \quad (24)$$

$$(1-P) L (1-P) = L_{int} - i R, \quad (25)$$

and

$$(1-P) L P = P L (1-P) = L_C, \quad (26)$$

and if L_C is rotationally invariant. As discussed in the introduction, the binary gas expansion and the dilute gas limit is taken as well established in this paper. Equations (24)-(26) are stated without further discussion.

The rotating frame approximation is now derived. Formal solution of Eq. (19) gives,

$$\phi^L(t) = -i \int_0^t \exp[-i(L_{int} - i R)S] L_C \phi^I(t-S) dS \quad (27)$$

with the usual assumption that $\phi^I(0) = 0$. The Markoffian approximation is,

$$\phi^I(t-S) = e^{iS\omega I^I Z} \phi^I(t) \quad (28)$$

or

$$\phi^I(t-S) = e^{-it\omega_I \hat{J}_Z} e^{+i\omega_I \hat{J}_Z 2S} \phi^I(S) . \quad (29)$$

Noting that $\hat{J}_Z \phi^I(S) = \hat{J}_Z \phi^I(S)$, and assuming that

$$e^{i\omega_I \hat{J}_Z t} L_C = L_C e^{i\omega_I \hat{J}_Z t} \quad (30)$$

gives,

$$e^{+i\omega_I \hat{J}_Z t} \phi^L(t) = -i \int_0^t \exp(-i(L_{int} - iR)S) L_C e^{+i2\omega_I \hat{J}_Z S} \phi^I(S) dS . \quad (31)$$

Taking the derivative with respect to t gives

$$+i\omega_I \hat{J}_Z e^{+i\omega_I \hat{J}_Z t} \phi^L(t) + e^{+i\omega_I \hat{J}_Z t} \frac{\partial \phi^L}{\partial t} = -i e^{-i(L_{int} - iR)t} L_C e^{+i2\omega_I \hat{J}_Z t} \phi^I(t) . \quad (32)$$

Since the collision operator R is a positive definite superoperator and accounts for relaxation, it is seen that the right-hand side of Eq. (32) decays to zero for sufficiently long times. Thus as $t \rightarrow \infty$,

$$i \frac{\partial \phi^L}{\partial t} = \omega_I \hat{J}_Z \phi^L , \quad (33)$$

which is the rotating frame approximation, Eq. (20).

Clearly no attempt has been made to justify the approximations used here, but they depend upon the weakness of the coupling, L_C , and are extensively discussed elsewhere.^{1,2,16}

IV. DISCUSSION

It is easily seen that taking the spin α' matrix element of Eq. (23) leads to the Redfield equations. Until this work, in the kinetic theory approach, the Redfield equations were not derived, it being assumed that the Bloch equation gave an adequate description of nuclear spin relaxation. This was inherent in the choice of the form of ϕ as⁷⁻⁹ $\phi = \underline{p} \cdot \underline{I} + \phi^I$. Thus at most only orientation off-diagonalities were included in ϕ^I . Furthermore, when treating the decay of $\langle I_Z \rangle$, ϕ^I becomes diagonal and Eq. (23) reduces to a Master equation. The modification to ϕ^I required in order to arrive at the Redfield equations is given in Eq. (12).

In the resolvent of Eq. (21) it is seen that the nuclear Zeeman Hamiltonian completely cancels. This is because $\omega_I \hat{J}_Z = \omega_I J_Z + L_{Z1}$. Consequently, the resolvent operates only in lattice space. The cancellation of L_{Z1} is a consequence of the choice that the motion of the nuclear spins are described only by a linear Zeeman hamiltonian, and that L_C is rotationally invariant.

Further, when solving the general non-Markoffian equation in the usual way²⁰ by use of Eq. (28) and setting $t = \infty$, the integral becomes,⁶

$$\begin{aligned} & \int_0^\infty P L(1-P) \exp[-i(1-P) L(1-P)S] (1-P) L P e^{iS\omega_I I_Z} dS \\ & = \int_0^\infty P L(1-P) \exp[-i(1-P) L(1-P)S + iS\omega_I \hat{J}_Z] (1-P) L P dS . \end{aligned}$$

Rotational invariance of $(1-P)L P$ is again assumed. This has the pleasing property of enabling the integral to be straightforwardly solved to give a resolvent.

Finally it is stated that the important aspect of Eq. (23) is not the form of the equation, but rather the explicit way in which binary collisions are taken into account through R . This is the essence of the kinetic theory approach. Equations (23) are not the Redfield equations as usually presented, but the Redfield equations valid for a dilute gas.

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