

# A comparison of generalized cumulant and projection operator methods in spin-relaxation theory\*

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The general spin-relaxation theories of Albers and Deutch and of Argyres and Kelley based on different projection operator methods, and the theory of Freed based on generalized cumulant expansions are compared. It is shown that the first two yield equivalent expressions for the time evolution of the spin density matrix. They are also found to be equivalent to a cumulant expansion based on *total* ordering of the cumulant operators (TTOC), which is different from the *partial* time ordering method (PTOC) used by Freed. The TTOC method is found to be the more convenient for the frequency domain (i.e., for calculating spectra), while the PTOC method is for time domain analyses. Examples of the use of the TTOC method are given. Useful expressions are given for the case where the lattice may be treated in terms of classical Markov processes, but, in general, it is found that for such cases the stochastic Liouville method is the more useful for computations.

## I. INTRODUCTION

Over the last several years, a variety of statistical-mechanical formalisms have been applied to general considerations of spin-relaxation theory. In particular, we note the work of Albers and Deutch<sup>1,2</sup> utilizing a projection operator formalism, the Argyres and Kelley<sup>3</sup> theory based on a different type of projection operator, and the work of Freed<sup>4,5</sup> based on generalized cumulant expansions.<sup>6,7</sup> Each of these theories yields a general description of the behavior of the spin density matrix for spins coupled to a lattice, but each description is embedded in its own formalism, and any equivalence between them is not evident. One of the objectives of the present work is to perform such a comparison to show the extent to which they are equivalent.

It is possible, first, to show the equivalence in the expressions for the spin-density matrix obtained using the two projection operator methods. We then study its relationship to the cumulant expansion method. Here the interesting question of the nature of the time ordering of the cumulant operators enters. It is found that the procedure used by Freed,<sup>4,5</sup> which we refer to as a Partial Time Ordered Cumulant (PTOC) has different characteristics than the projection operator methods. However, it is possible to define another time-ordering scheme, referred to as a Total Time Ordered Cumulant (TTOC), which is then found to be equivalent to the projection operator methods.

It is then shown how the TTOC method may be effectively utilized in dealing with spin relaxation problems. Its utility relative to the PTOC method is compared in both the frequency and time domains. Our results are given both for general descriptions of the lattice as well as for the particularly useful case where the lattice motion is modeled as a classical stationary Markov process. We compare, for the latter case, the cumulant (and equivalent projection operator) methods with the very useful stochastic Liouville equation (SLE),<sup>8-11</sup> which may be derived by summing the generalized moment expan-

sions (upon which the cumulant expansions are based) to all orders.<sup>5</sup>

## II. PROJECTION OPERATOR METHODS

We explicitly consider the case of a single spin relaxation through contact with a thermal bath or lattice. The Hamiltonian for such a system is:

$$H = H_0 + \lambda H_1 = H_s + H_l + \lambda H_1, \quad (2.1)$$

where  $H_s$  is the Hamiltonian for the spin in the presence of a static magnetic field (i.e., is independent of the lattice),  $H_l$  is the Hamiltonian describing the lattice degrees of freedom, and  $H_1$  is the interaction of the spin and lattice with  $\lambda$  a measure of its magnitude.

The projection operator methods of Argyres and Kelley<sup>3</sup> and of Albers and Deutch<sup>1,2</sup> provide two approaches for extracting the relevant dynamics of the spin subsystem. Starting from the equation of motion for the density matrix of the system  $\rho(t)[\hbar = 1]$ ,

$$\dot{\rho}(t) = -i[H, \rho(t)] \equiv -iH^* \rho(t) \equiv -iL\rho(t), \quad (2.2)$$

where  $L \equiv H^* \equiv i[H, \dots]$  is the Liouville operator of the system, Argyres and Kelley derive an equation of motion for the spin density matrix  $\sigma(t)$  that is obtained from  $\rho(t)$  by taking a trace over lattice variables

$$\sigma(t) = \text{Tr}_l[\rho(t)]. \quad (2.3)$$

These authors employ the projection operator

$$P = \rho_l \text{Tr}_l, \quad (2.4)$$

where  $\rho_l$  is the equilibrium lattice density matrix

$$\rho_l = \exp(-\beta H_l) \{ \text{Tr}_l[\exp(-\beta H_l)] \}^{-1}, \quad (2.5)$$

to obtain the equation of motion<sup>3</sup>

$$\dot{\sigma}(t) = -iL_s \sigma(t) - \lambda^2 \int_0^t d\tau \text{Tr}_l[L' e^{-i(1-P)L\tau} L' \rho_l] \sigma(t-\tau), \quad (2.6)$$

where  $L_s \equiv H_s^*$ ,  $L' \equiv H_1^*$ ; furthermore  $L_0 = L_s + L_l$ .

The alternative approach of Albers and Deutch<sup>1,2</sup> has

the advantage of retaining explicit reference to the lattice variables. These authors obtain an equation of motion for the generating function

$$G_{\alpha\alpha'}(t) \equiv e^{iHt} |\alpha'\rangle \langle \alpha| e^{-iHt}, \quad (2.7)$$

where  $|\alpha\rangle$  denotes an eigenstate of  $H_s$  by use of the projection operator

$$P' = \text{Tr}_1 \rho_1 \equiv \langle \dots \rangle. \quad (2.8)$$

The resulting equation of motion is<sup>1,2</sup>

$$\begin{aligned} \dot{G}_{\alpha\alpha'}(t) = & -i\omega_{\alpha\alpha'} G_{\alpha\alpha'}(t) + K_{\alpha\alpha'}(t, \lambda) \\ & + \lambda^2 \sum_{\beta, \beta'} \int_0^t d\tau \langle \beta' | F_{\alpha\alpha'}(t, \lambda) | \beta \rangle G_{\beta\beta'}(t - \tau), \end{aligned}$$

where  $\omega_{\alpha\alpha'} = (E_\alpha - E_{\alpha'})$  and  $E_\alpha$  is the energy of spin state  $|\alpha\rangle$ ,  $K_{\alpha\alpha'}(t, \lambda)$  is a random "force" given by

$$K_{\alpha\alpha'}(t) = \exp[i(1 - P')t] i\lambda L' G_{\alpha\alpha'}(0), \quad (2.9a)$$

and the damping kernel is

$$\langle \beta' | F_{\alpha\alpha'}(t, \lambda) | \beta \rangle = \lambda^{-1} \langle \beta' | iL' K_{\alpha\alpha'}(t, t) | \beta \rangle. \quad (2.9b)$$

All spin quantities of interest can be extracted from  $G_{\alpha\alpha'}(t)$ . In particular the equation of motion for  $\sigma_{\alpha\alpha'}(t)$  obtained from Eq. (2.9) for  $G_{\alpha\alpha'}(t)$  by the definition

$$\sigma_{\alpha\alpha'}(t) = \text{Tr}[\rho(0)G_{\alpha\alpha'}(t)]$$

is

$$\begin{aligned} \dot{\sigma}_{\alpha\alpha'}(t) = & -i\omega_{\alpha\alpha'} \sigma_{\alpha\alpha'}(t) \\ & + \lambda^2 \sum_{\beta, \beta'} \int_0^t dt \langle \beta' | F_{\alpha\alpha'}(t, \lambda) | \beta \rangle \sigma_{\beta\beta'}(t - t). \end{aligned} \quad (2.10)$$

In both projection operator derivations the Hamiltonian has been partitioned so that  $\langle H' \rangle = 0$  and the usual assumption for the initial spin density matrix  $\rho(0) = \rho_1 \sigma(0)$  has been made.

In order to examine the equivalence of the two projection operator equations we rewrite Eq. (2.10) as

$$\begin{aligned} \dot{\sigma}_{\alpha\alpha'}(t) = & -i\omega_{\alpha\alpha'} \sigma_{\alpha\alpha'}(t) \\ & - \lambda^2 \int_0^t d\tau \text{Tr}_1 \text{Tr}_s \rho_1 \sigma(t - \tau) L' e^{i(1 - P')L\tau} |\alpha\rangle \langle \alpha|. \end{aligned} \quad (2.11)$$

Let us expand  $e^{i(1 - P')L\tau}$ ; notice that  $\text{Tr}_1 \text{Tr}_s = \text{Tr}$  over all the degrees of freedom:

$$\begin{aligned} \dot{\sigma}_{\alpha\alpha'}(t) = & \langle \alpha | -iL_s \sigma(t) | \alpha' \rangle - \lambda^2 \int_0^t d\tau \\ & \times \text{Tr} \rho_1 \sigma(t - \tau) L' \sum_{n=0}^{\infty} \frac{[i(1 - P)L\tau]^n}{n!} L' | \alpha' \rangle \langle \alpha|. \end{aligned} \quad (2.12)$$

It is easy to show that for any two matrices  $A$  and  $B$  one has the trace properties:

$$\text{Tr} ALB = -\text{Tr}(LA)B, \quad (2.13a)$$

$$\text{Tr} AP'B = \text{Tr}(PA)B, \quad (2.13b)$$

$$\text{Tr} A(1 - P')LB = -\text{Tr}[L(1 - P)A]B. \quad (2.13c)$$

We may apply these identities to the  $n$ th term in Eq. (2.12) to show that

$$\text{Tr} \rho_1 \sigma(t - \tau) L' \frac{[i(1 - P')L\tau]^n}{n!} L' | \alpha' \rangle \langle \alpha|$$

$$= \text{Tr} \left\{ L' \frac{[-iL\tau(1 - P)]^n}{n!} L' \rho_1 \sigma(t - \tau) \right\} | \alpha' \rangle \langle \alpha|. \quad (2.14)$$

We notice now that because  $\text{Tr}_1 \rho_1 H_1 = 0$  one has

$$[-iL\tau(1 - P)] L' \rho_1 \sigma(t - \tau) = -iL\tau L' \rho_1 \sigma(t - \tau), \quad (2.15a)$$

and

$$\text{Tr}_1 L'B = \text{Tr}(1 - P)L'B. \quad (2.15b)$$

This enables us to rewrite Eq. (2.14) after some manipulation as:

$$\langle \alpha | \text{Tr}_1 L' \frac{[-i(1 - P)L\tau]^n}{n!} L' \rho_1 \sigma(t - \tau) | \alpha' \rangle, \quad (2.16)$$

where we have performed the operation  $\text{Tr}_s$ . This result may be substituted back into Eq. (2.12) to yield

$$\begin{aligned} \dot{\sigma}_{\alpha\alpha'}(t) = & \langle \alpha | -iL_s \sigma(t) | \alpha' \rangle - \lambda^2 \int_0^t d\tau \\ & \times \langle \alpha | \text{Tr}_1 L' \sum_{n=0}^{\infty} \frac{[-i(1 - P)L\tau]^n}{n!} L' \rho_1 \sigma(t - \tau) | \alpha' \rangle, \end{aligned} \quad (2.17)$$

which may be rewritten in operator form as

$$\dot{\sigma}_{\alpha\alpha'}(t) = -iL_s \sigma(t) - \lambda^2 \int_0^t d\tau \text{Tr}_1 L' e^{-i(1 - P)L\tau} L' \rho_1 \sigma(t - \tau) \quad (2.18)$$

Eq. (2.18) is precisely the expression obtained by Argyres and Kelley,<sup>3</sup> utilizing the more traditional projection operator given by Eq. (2.4).

Thus both projection operator methods are seen to yield equivalent expressions for  $\sigma(t)$  as already pointed out in a general sense.<sup>2</sup> A more useful form for computation (as well as for intercomparison with cumulant methods) may be obtained as follows. We utilize the operator identity

$$e^{-i(1 - P)L\tau} = e^{-iL_0\tau} - i \int_0^\tau d\tau_1 e^{-iL_0(\tau - \tau_1)} (\lambda L' - PL) e^{-i(1 - P)L\tau_1} \quad (2.19)$$

to show

$$\begin{aligned} (\lambda L' - PL) e^{-i(1 - P)L\tau_1} L' \rho_1 \sigma(t - \tau) \\ = \lambda(1 - P) L' e^{-i(1 - P)L\tau_1} \rho_1 \sigma(t - \tau), \end{aligned} \quad (2.20)$$

since

$$PL_1 A = 0 \quad (2.21a)$$

and

$$\begin{aligned} PL_s e^{-i(1 - P)L\tau_1} L' \rho_1 \sigma(t - \tau) &= L_s P e^{-i(1 - P)L\tau_1} L' \rho_1 \sigma(t - \tau) \\ &= L_s P \left( 1 + \sum_{n=1}^{\infty} \frac{[-i(1 - P)L\tau_1]^n}{n!} \right) \\ &\quad \times L' \rho_1 \sigma(t - \tau) \end{aligned} \quad (2.21b)$$

so

$$PL_s e^{-i(1 - P)L\tau_1} L' \rho_1 \sigma(t - \tau) = L_s PL' \rho_1 \sigma(t - \tau) = 0. \quad (2.22)$$

If we iterate the operator identity and substitute into Eq. (2.18) we get

$$\begin{aligned} \dot{\sigma}(t) = & -iL_S\sigma(t) - \lambda^2 \int_0^t d\tau \text{Tr}_1 L' \left[ e^{-iL_0\tau} + \sum_{n=1}^{\infty} (-i\lambda)^n \int_0^\tau d\tau_1 \cdots \int_0^{\tau_{n-1}} d\tau_n \right. \\ & \left. \times e^{-iL_0(\tau-\tau_1)}(1-P)L'e^{-iL_0(\tau_1-\tau_2)}(1-P)L' \cdots e^{-iL_0(\tau_{n-1}-\tau_n)}(1-P)L'e^{-iL_0\tau_n} \right] L' \rho_I \sigma(t-\tau). \end{aligned} \quad (2.23)$$

We now transform to the interaction representation by

$$\sigma^*(t) = e^{iL_S t} \sigma(t) \quad (2.24a)$$

$$L'(t) \equiv e^{+iL_0 t} L' e^{-iL_0 t}, \quad (2.24b)$$

and utilize the facts that

$$\text{Tr}_1 e^{iL_1 t} A = \text{Tr}_1 e^{iH_1 t} A e^{-iH_1 t} = \text{Tr}_1 A \quad (2.25a)$$

and

$$e^{-iL_1 t} \rho_I = \rho_I, \quad (2.25b)$$

(since  $\rho_I$  is the unique equilibrium distribution for the unperturbed lattice) to obtain

$$\begin{aligned} \dot{\sigma}^*(t) = & -\lambda^2 \int_0^t d\tau \text{Tr}_1 L'(t) \left[ 1 + \sum_{n=1}^{\infty} (-i\lambda)^n \int_0^\tau d\tau_1 \cdots \int_0^{\tau_{n-1}} d\tau_n \right. \\ & \left. \times L'(t-\tau+\tau_1)(1-P)L'(t-\tau+\tau_2) \right. \\ & \left. \cdots (1-P)L'(t-\tau+\tau_n) \right] L'(t-\tau) \rho_I \sigma^*(t-\tau). \end{aligned} \quad (2.26)$$

This result will be compared with the cumulant methods.

### III. TOTAL TIME-ORDERED GENERALIZED CUMULANT METHOD

We start with the quantum-mechanical Liouville equation (2.2). We transform it to the interaction representation by:

$$\rho^*(t) = e^{iL_0 t} \rho(t) \quad (3.1)$$

to obtain

$$\dot{\rho}^*(t) = -i\lambda L'(t) \rho^*(t), \quad (3.2)$$

where  $L'(t)$  is again given by Eq. (2.24b). The solution to Eq. (3.2) is given by the expansion:

$$\begin{aligned} \rho^*(t) = & \rho^*(0) + \sum_{n=1}^{\infty} (-i\lambda)^n \int_0^t dt_1 \cdots \int_0^{t_{n-1}} \\ & \times dt_n L'(t_1) \cdots L'(t_n) \rho^*(0). \end{aligned} \quad (3.3)$$

We now take the trace over lattice states,  $\text{Tr}_1$ , and again make the usual approximation that the lattice states are initially at equilibrium [cf. Eq. (2.6)]. Then Eq. (3.3) becomes the "generalized moment expansion"<sup>4,5</sup>:

$$\sigma^*(t) = \sum_{n=0}^{\infty} M_n(t) \sigma(0) \quad (3.4)$$

where the  $n$ th generalized moment is

$$\begin{aligned} M_n(t) = & (-i\lambda)^n \int_0^t dt_1 \cdots \int_0^{t_{n-1}} dt_n \\ & \times \text{Tr}_1 L'(t_1) \cdots L'(t_n) \rho_I \sigma(0) \quad n \geq 1, \end{aligned} \quad (3.5a)$$

$$M_0(t) = 1. \quad (3.5b)$$

In the cumulant method we seek an operator  $\exp_0 K(t)$ , where the subscript 0 prescribes a time ordering, such that

$$\sigma^*(t) = [\exp_0 K(t)] \sigma(0). \quad (3.6)$$

One choice of time-ordering was utilized previously.<sup>4,5</sup> Now let us assume  $K(t)$  to be of the form:

$$K(t) = \sum_{m=1}^{\infty} \lambda^m \int_0^t dt_1 \cdots \int_0^{t_{m-1}} dt_m \theta_m(t_1, \dots, t_m), \quad (3.7)$$

where the cumulants  $\theta_m(t_1, \dots, t_m)$  are defined in terms of an ordering prescription such that

$$\begin{aligned} \exp_0 K(t) = & 1 + \sum_{m=1}^{\infty} \lambda^m \int_0^t dt_1 \cdots \int_0^{t_{m-1}} dt_m \theta_m(t_1, \dots, t_m) \\ & + \sum_{m,p=1}^{\infty} \lambda^{m+p} \int_0^t dt_1 \cdots \int_0^{t_{m-1}} dt_m \int_0^{t_m} dt_{m+1} \cdots \int_0^{t_{m+p-1}} dt_{m+p} \theta_m(t_1, \dots, t_m) \theta_p(t_{m+1}, \dots, t_{m+p}) \\ & + \sum_{m,p,s=1}^{\infty} \lambda^{m+p+s} \int_0^t dt_1 \cdots \int_0^{t_{m-1}} dt_m \int_0^{t_m} dt_{m+1} \cdots \int_0^{t_{m+p-1}} dt_{m+p} \int_0^{t_{m+p}} dt_{m+p+1} \\ & \cdots \int_0^{t_{m+p+s-1}} dt_{m+p+s} \theta_m(t_1, \dots, t_m) \theta_p(t_{m+1}, \dots, t_{m+p}) \theta_s(t_{m+p+1}, \dots, t_{m+p+s}). \end{aligned} \quad (3.8)$$

The  $\theta_m$ 's may be determined by equating like powers of  $\lambda$  for Eqs. (3.5a) and (3.7) to yield

$$\theta_1(t_1) = -i \text{Tr}_1 L'(t_1) \rho_I, \quad (3.9a)$$

$$\theta_2(t_1, t_2) = -\text{Tr}_1 L'(t_1) (1 - \rho_I \text{Tr}_1) L'(t_2) \rho_I, \quad (3.9b)$$

$$\begin{aligned} \theta_3(t_1, t_2, t_3) = & i \text{Tr}_1 L'(t_1) (1 - \rho_I \text{Tr}_1) \\ & \times L'(t_2) (1 - \rho_I \text{Tr}_1) L'(t_3) \rho_I, \end{aligned} \quad (3.9c)$$

$$\theta_4(t_1, t_2, t_3, t_4) = \text{Tr}_1 L'(t_1) (1 - \rho_I \text{Tr}_1) L'(t_2) (1 - \rho_I \text{Tr}_1)$$

$$\times L'(t_3) (1 - \rho_I \text{Tr}_1) L'(t_4) \rho_I, \quad (3.9d)$$

and the general term is

$$\begin{aligned} \theta_n(t_1, \dots, t_n) = & (-i)^n \text{Tr}_1 L'(t_1) (1 - \rho_I \text{Tr}_1) \\ & \cdots L'(t_{n-1}) (1 - \rho_I \text{Tr}_1) L'(t_n) \rho_I. \end{aligned} \quad (3.10)$$

Let us now assume, as before, that we have partitioned  $H$  such that  $\text{Tr}_1 \rho_I H_1 = 0$ . Then  $\theta_1(\tau) = 0$ . We now take the time derivative of Eq. (3.7), and after rear-

ranging terms obtain the result:

$$\frac{\partial}{\partial t} \exp_0 K(t) = \sum_{n=1}^{\infty} \lambda^{n+1} \int_0^t dt_1 \cdots \int_0^{t_{n-1}} dt_n \theta_{n+1}(t, t_1, \dots, t_n) \exp_0 K(t_n) \tag{3.11}$$

We now change the order of integration for the last two integrals, i. e.,

$$\int_0^{t_{n-2}} dt_{n-1} \int_0^{t_{n-1}} dt_n = \int_0^{t_{n-2}} dt_n \int_{t_n}^{t_{n-1}} dt_{n-1}$$

and subsequently repeat this integral switch to obtain

$$\int_0^t dt_1 \cdots \int_0^{t_{n-1}} dt_n = \int_0^t dt_n \int_{t_n}^t dt_1 \int_{t_n}^{t_1} dt_2 \cdots \int_{t_n}^{t_{n-3}} dt_{n-2} \int_{t_n}^{t_{n-2}} dt_{n-1}$$

We now define new time variables:

$$\tau \equiv t - t_n, \quad t'_1 = t_1 - (t - \tau)$$

or generally

$$t'_m = t_m - (t - \tau)$$

This enables us to rewrite Eq. (3.11) as (after dropping the primes)

$$\frac{\partial}{\partial t} \exp_0 K(t) = \lambda^2 \int_0^t d\tau \left\{ \theta_2(t, t - \tau) + \sum_{n=1}^{\infty} \lambda^n \int_0^{\tau} dt_1 \cdots \int_0^{t_{n-1}} dt_n \right.$$

$$\left. \times \theta_{n+2}(t, t - \tau + t_1, \dots, t - \tau + t_n, t - \tau) \right\} \exp_0 K(t - \tau) \tag{3.12}$$

We now take the time derivative of Eq. (3.6):

$$\dot{\sigma}^*(t) = \left[ \frac{\partial}{\partial t} \exp_0 K(t) \right] \sigma(0), \tag{3.13}$$

and substitute Eqs. (3.12) and (3.10) into Eq. (3.13) and utilize the fact that  $\text{Tr}_1 \rho_1 H_1 = 0$  to obtain

$$\begin{aligned} \dot{\sigma}^*(t) = & -\lambda^2 \int_0^t d\tau \text{Tr}_1 L'(t) \left\{ 1 + \sum_{n=1}^{\infty} (-i\lambda)^n \int_0^{\tau} dt_1 \right. \\ & \cdots \int_0^{t_{n-1}} dt_n L'(t - \tau + t_1) (1 - \rho_1 \text{Tr}_1) L'(t - \tau + t_2) \\ & \left. \cdots (1 - \rho_1 \text{Tr}_1) L'(t - \tau + t_n) \right\} L'(t - \tau) \rho_1 \sigma^*(t - \tau), \end{aligned} \tag{3.14}$$

which is just Eq. (2.26). This demonstrates the equivalence between the TTOC and the projection operator methods.

A very useful form for the TTOC method is obtained by first substituting Eq. (3.11) into Eq. (3.13) and then utilizing Eq. (3.6) to yield

$$\dot{\sigma}^*(t) = \sum_{n=1}^{\infty} \lambda^{n+1} \int_0^t dt_1 \cdots \int_0^{t_{n-1}} dt_n \theta_{n+1}(t, t_1, \dots, t_n) \sigma^*(t_n) \tag{3.15}$$

We may now transform Eq. (3.15) back to the Schrödinger representation [cf. Eqs. (2.23) and (2.26)] and then use Eq. (3.10):

$$\begin{aligned} \dot{\sigma}(t) = & -iL_s \sigma(t) + \sum_{n=1}^{\infty} \lambda^{n+1} \int_0^t dt_1 \cdots \int_0^{t_{n-1}} dt_n e^{-iL_s t} \theta_{n+1}(t, t_1, \dots, t_n) e^{+iL_s t_n} \sigma(t_n) = -iL_s \sigma(t) \\ & + \sum_{n=1}^{\infty} (-i\lambda)^{n+1} \int_0^t dt_1 \cdots \int_0^{t_{n-1}} dt_n \text{Tr}_1 L' e^{-iL_0(t-t_1)} (1-P) L' e^{-iL_0(t_1-t_2)} (1-P) L' \cdots e^{-iL_0(t_{n-1}-t_n)} (1-P) L' \rho_1 \sigma(t_n). \end{aligned} \tag{3.16}$$

This multiple-time integral is readily Fourier-Laplace transformed to give

$$[i(\omega + L_s) - \mathcal{G}(i\omega)] \sigma(\omega) = \sigma(0), \tag{3.17}$$

or

$$\sigma(\omega) = [i(\omega + L_s) - \mathcal{G}(i\omega)]^{-1} \sigma(0), \tag{3.17'}$$

with

$$\mathcal{G}(i\omega) = \sum_{n=1}^{\infty} (-i\lambda)^{n+1} \text{Tr}_1 L' \left[ \frac{1}{i\omega + iL_0} (1-P) L' \right]^n \rho_1 \tag{3.18}$$

This is a generalized perturbation scheme in  $L'$ . Note that the inclusion of the  $(1-P)$  operator is just the concept of "connected cumulants" such that the initial lattice state (i. e., the equilibrium  $\rho_1$ ) does not appear in any of the intermediate states. (The result given here does not necessarily require that  $\text{Tr}_1 H' \rho_1 = 0$  so the sum in Eq. (3.18) may in general include the  $n=0$  term.)

For realistic problems, one does not attempt to completely describe the lattice states. Instead we first define the operators

$$\hat{H}'(t) \equiv e^{iL t} H_1, \tag{3.19}$$

$$\hat{L}'(t) \equiv e^{iL t} L' e^{-iL t}, \tag{3.20}$$

and refer to  $\hat{H}'(t)$  as the randomly fluctuating perturbation resulting from the complex lattice motions. This is equivalent to the usual semiclassical approach.<sup>4,5</sup> Then Eq. (3.16) becomes

$$\begin{aligned} \dot{\sigma}(t) = & -iL_s \sigma(t) + \sum_{n=1}^{\infty} (-i\lambda)^{n+1} \int_0^t dt_1 \cdots \int_0^{t_{n-1}} dt_n \text{Tr}_1 \hat{L}'(t) \\ & \times e^{-iL_s(t-t_1)} (1-P) \hat{L}'(t) e^{-iL_s(t_1-t_2)} (1-P) \hat{L}'(t_2) \\ & \cdots e^{-iL_0(t_{n-1}-t_n)} (1-P) \hat{L}'(t_n) \rho_1 \sigma(t_n), \end{aligned} \tag{3.21}$$

where we now let

$$\text{Tr}_1 \equiv \langle P_0 |, \tag{3.22a}$$

$$\rho_1 \equiv | P_0 \rangle, \tag{3.22b}$$

so

$$P = | P_0 \rangle \langle P_0 |, \tag{3.22c}$$

and we have introduced the bra-ket notation such that  $\langle P_0 | Q | P_0 \rangle$  is the average of  $Q$  over the unique equilibrium state  $P_0$ . This is closely related to the usual semiclassical expansion in terms of the  $M_n(t)$ <sup>4,5</sup> except for the  $(1-P)$  terms, which, as we have seen, define the cumulant averaging. The explicit time dependence of the "random operator"  $\hat{L}'(t)$  may be dealt with by

making specific assumptions about the random stochastic process. In particular, we assume a Markov process, such that

$$\frac{\partial}{\partial t} P(\Omega, t) = -\Gamma_{\Omega} P(\Omega, t), \quad (3.23)$$

where  $P(\Omega, t)$  is the probability distribution at time  $t$  for the Markov process specified for the collection of lattice variables represented by  $\Omega$ ; and  $\Gamma_{\Omega}$  is the time-independent Markov operator.

Then we have

$$\Gamma_{\Omega} |P_0(\Omega)\rangle = 0, \quad (3.24a)$$

$$\langle P_0(\Omega) | \Gamma_{\Omega} = 0, \quad (3.24b)$$

for the bra and ket vectors corresponding to the equilibrium distribution. Furthermore we assume  $\Gamma_{\Omega}$  has a

complete set of eigenfunctions  $G_m(\Omega)$  such that

$$\Gamma_{\Omega} |G_m(\Omega)\rangle = E_m |G_m(\Omega)\rangle, \quad (3.25a)$$

and

$$\langle G_m(\Omega) | \Gamma_{\Omega} = E_m \langle G_m(\Omega) | \Gamma_{\Omega}. \quad (3.25b)$$

If we now recognize that Eq. (3.23) has a formal solution for the conditional probability or Green's function  $P(\Omega_0 | \Omega, t)$  of

$$P(\Omega_0 | \Omega, t) = e^{-\Gamma t} \delta(\Omega - \Omega_0), \quad (3.26)$$

so that for any function of  $\Omega$  or  $A(\Omega)$ :

$$e^{-\Gamma t} A(\Omega) = \int P(\Omega_t | \Omega, t) A(\Omega_t) d\Omega_t. \quad (3.27)$$

Then by analogy to the discussion by Freed<sup>12</sup> one has

$$\begin{aligned} \dot{\sigma}(t) = & -iL_s \sigma(t) + \sum_{n=1}^{\infty} (-i\lambda)^{n+1} \int_0^t dt_1 \cdots \int_0^{t_{n-1}} dt_n \langle P_0 | L' e^{-i(t-t_1)(L_s + \Gamma)} \\ & \times (1 - |P_0\rangle\langle P_0|) L' e^{-i(t_1-t_2)(L_s + \Gamma)} (1 - |P_0\rangle\langle P_0|) L' \cdots e^{-i(t_{n-1}-t_n)(L_s + \Gamma)} (1 - |P_0\rangle\langle P_0|) L' | P_0 \rangle \sigma(t_n), \end{aligned} \quad (3.28)$$

with Fourier-Laplace transform again given by Eq. (3.17), but now

$$\begin{aligned} \mathcal{G}(i\omega) = & \sum_{n=1}^{\infty} (-i\lambda)^{n+1} \langle P_0 | L' \left[ \frac{1}{i\omega + iL_s + \Gamma} (1 - |P_0\rangle\langle P_0|) L' \right]^n | P_0 \rangle \\ = & \sum_{n=1}^{\infty} \sum'_{\substack{m_1, m_2, \\ \dots, m_n=1}} \langle P_0 | L' | G_{m_1} \rangle \langle G_{m_1} | \frac{1}{i\omega + iL_s + E_{m_1}} L' | G_{m_2} \rangle \cdots \langle G_{m_n} | \frac{1}{i\omega + iL_s + E_{m_n}} L' | P_0 \rangle, \end{aligned} \quad (3.29)$$

where the prime restricts the summations over the C.O.N. set of  $|G_{m_i}\rangle$  to exclude  $|G_0\rangle = |P_0\rangle$ . Again this is the concept of connected cumulants as applied to the Markov process. [Also we use the fact that  $\Gamma$  is diagonal in the  $G_m$  representation in obtaining the second equality of Eq. (3.29).]

We note here that expansion of the generalized moments, instead of the cumulants, has already been shown to yield the "stochastic-Liouville equation" (SLE)<sup>8-11</sup>

$$\sigma(\omega) = \langle P_0 | [i\omega + i(L_s + L') + \Gamma_{\Omega}]^{-1} | P_0 \rangle \sigma(0), \quad (3.30)$$

or in operator form with respect to lattice variables  $\Omega$ :

$$\dot{\sigma}(\Omega, t) = -[i(L_s + L') + \Gamma_{\Omega}] \sigma(\Omega, t). \quad (3.31)$$

Equation (3.31) (or its Fourier-Laplace transform) has now been used extensively in a wide variety of applications, and has been shown to be a very powerful method for problems involving spin-dynamics.<sup>9-11,13</sup> It is clear that Eq. (3.30) must be equivalent to Eqs. (3.17) and (3.29), since, in general, the generalized cumulant and moment expansions are equivalent when carried out to all orders.<sup>6</sup> We comment further on this in the next section.

#### IV. METHODS OF SOLUTION UTILIZING TTOC APPROACH

We have for an unsaturated lineshape<sup>10,11</sup>

$$I(\omega) \propto \text{ReTr}_s \int_0^{\infty} e^{-i\omega t} \langle S_x(t) S_x(0) \rangle = \text{ReTr}_s S_x(i\omega) S_x(0) = \text{ReTr}_s [i(\omega - L_s) - \mathcal{G}^*(\omega)]^{-1} S_x(0) S_x(0), \quad (4.1)$$

where  $\mathcal{G}^*(\omega)$  is a partial complex conjugate of  $\mathcal{G}(\omega)$  (i.e., the  $i\omega$  terms do not change sign). If we consider a simple line for the transition  $\alpha \rightarrow \alpha'$  with  $(L_s)_{\alpha\alpha'}, \alpha\alpha' = \omega_0$ , then we have

$$I(\omega) \propto \text{Re} [i(\omega - \omega_0) - \mathcal{G}^*(\omega)_{\alpha\alpha'}, \alpha\alpha'}]^{-1} S_x(0)_{\alpha\alpha'} S_x(0)_{\alpha'\alpha}, \quad (4.2)$$

and

$$\begin{aligned} \mathcal{G}^*(i\omega)_{\alpha\alpha', \beta\beta'} = & \sum_{n=1}^{\infty} \sum'_{\substack{m_1, m_2, \\ \dots, m_n=1}} \sum_{\text{all } r_1, r'_1} (+i\lambda)^{n+1} \langle P_0 | L'_{\alpha\alpha', r_1 r'_1} | G_{m_1} \rangle \\ & \times \langle G_{m_1} | \frac{1}{i(\omega - \omega_1) + E_{m_1}} L'_{r_1 r'_1, r_2 r'_2} | G_{m_2} \rangle \cdots \langle G_{m_n} | \frac{1}{i(\omega - \omega_n) + E_{m_n}} L'_{r_n r'_n, \beta\beta'} | P_0 \rangle, \end{aligned} \quad (4.3)$$

where  $\omega_i \equiv L_{\beta_i \gamma_i \beta'_i \gamma'_i}$ . In particular, for a purely secular perturbation, i. e.,  $L'_{\alpha\alpha', \beta\beta'} = \omega'(\Omega) \delta_{\alpha, \beta} \delta_{\alpha', \beta'}$  one has

$$\mathcal{G}^*(i\omega)_{\alpha\alpha', \alpha\alpha'} = \sum_{n=1}^{\infty} \sum_{\substack{m_1, m_2, \\ \dots, m_n=1}}^{\infty} (i\lambda)^{n+1} \langle P_0 | \omega'(\Omega) | G_{m_1} \rangle \langle G_{m_1} | \frac{\omega'(\Omega)}{i(\omega - \omega_0) + E_{m_1}} | G_{m_2} \rangle \dots \langle G_{m_n} | \frac{\omega'(\Omega)}{i(\omega - \omega_0) + E_{m_n}} | P_0 \rangle. \quad (4.4)$$

We have applied Eq. (4.4) through fourth order (i. e.,  $n \leq 4$ ) to the two simple models of 2 jumps and rotational diffusion used by Freed<sup>4</sup> (cf. Sec. V) and have found, (as expected) that the results agree with those from the PTOC method given there. Typical selection rules on the spatial "matrix elements"  $\langle G_{m_i} | \omega'(\Omega) | G_{m_j} \rangle$  such as those embodied in the 3<sub>j</sub> symbols for rotational diffusion models, greatly reduce the number of terms in the sums over the  $m_i$  (cf. Sec. V).

When the line is not a simple one, then the operator properties of  $L_s$  and  $\mathcal{G}^*(\omega)$  in spin-(super)space must be fully considered. Then Eq. (4.1) yields

$$I(\omega) \propto \sum_{\substack{\alpha, \alpha' \\ \beta, \beta'}} \text{Re}[i(\omega - L_s) + \mathcal{G}^*(\omega)]^{-1}_{\alpha\alpha', \beta\beta'} (S_x)_{\beta\beta'} (S_x)_{\alpha'\alpha}. \quad (4.5)$$

It is of course, better to solve:

$$\sum_{\beta\beta'} [i(\omega - \omega_{\alpha\alpha'}) \delta_{\alpha\beta} \delta_{\alpha'\beta'} + \mathcal{G}^*(\omega)_{\alpha\alpha', \beta\beta'}] (S_x)_{\beta\beta'} = S_x \alpha\alpha' \quad (4.6)$$

for  $S_x(i\omega)_{\beta\beta'}$ , defined in Eq. (4.1). Equation (4.6) is solved by first calculating each  $\mathcal{G}^*(\omega)_{\alpha\alpha', \beta\beta'}$  of interest according to Eq. (4.3), and then diagonalizing the coupled algebraic equations resulting from Eq. (4.6).

The major problem for this method compared to the usual approaches for dealing with the stochastic Liouville equation<sup>9-11</sup> is the complexity of the summations over the  $m_i$  and  $\beta_i, \beta'_i$  for large  $n$  in problems involving a variety of transitions and perturbation terms in  $L'$ . The SLE solutions, however, involve a simple (though sometimes very large) matrix array which usually may be diagonalized once, independent of the magnitude of the sweep variable  $(\omega - \omega_0)$ . However, the structure of  $\mathcal{G}^*(\omega)$  exposes the structure of the important terms in the actual solution of the spectrum, and it may sometimes be useful from this point of view.

We note, in this context, a somewhat related expansion that comes from the SLE expression<sup>10,11</sup>:

$$S_x(i\omega) = [i(\omega - H^x) + \Gamma]^{-1} S_x(0), \quad (4.7a)$$

or

$$\langle S_x(i\omega) \rangle = \langle P_0 | [i(\omega - H^x) + \Gamma]^{-1} | P_0 \rangle S_x(0). \quad (4.7b)$$

A resolvent-type perturbation expansion<sup>14</sup> yields

$$S_x(i\omega) = \langle P_0 | \sum_{m=0}^{\infty} \left( \frac{1}{i(\omega - H^x) + \Gamma} [iH_1(\Omega)^x] \right)^m \frac{1}{i(\omega - H^x) + \Gamma} | P_0 \rangle S_x(0), \quad (4.8)$$

However, this perturbation scheme must be used with care, since it does not incorporate the connected-cumulant aspect, and some of the denominators will go to zero at the resonance frequencies. However, van Vleck-type perturbation schemes are very effective in

handling degeneracies, etc.<sup>9,13</sup> Note that Eq. (4.8) is simply equivalent to the Laplace transform of the generalized moment expansion.<sup>12</sup> In this context, a resolvent-type expansion can be rearranged [cf. Ref. 14, Eq. (4.372)] to be the formal equivalent of Eqs. (3.17) and (3.18) or (3.29). This clarifies the equivalence between the SLE and the TTOC results for Markov processes that have been obtained here.

### V. EXAMPLES USING THE TTOC METHOD

We illustrate the TTOC (or equivalent projection operator) methods with the two simple examples given by Freed.<sup>4</sup>

(1) Two Jump Model, Classical Lattice, Markov Process. Here we have two states  $A$  and  $B$  with *a priori* probabilities:

$$W_A + W_B = 1, \quad (5.1)$$

and with mean lifetimes  $\tau_A$  and  $\tau_B$ . The conditional probabilities are then

$$P(i|j, \tau) = W_j [1 - e^{-k\tau}] + e^{-k\tau} \delta_{ij}, \quad i, j = A, B \quad (5.2)$$

where  $k = \tau_A^{-1} + \tau_B^{-1}$ . It is more convenient, however, to introduce the Markov operator  $\Gamma$  according to:

$$\dot{P} = \Gamma P, \quad (5.3)$$

such that

$$\Gamma = \begin{pmatrix} -\tau_A^{-1} & \tau_B^{-1} \\ \tau_A^{-1} & -\tau_B^{-1} \end{pmatrix} \quad (5.4)$$

in the bases of eigenkets  $|A\rangle$  and  $|B\rangle$ . It is generally useful to symmetrize  $\Gamma$  according to the transformation  $\tilde{\Gamma} = P_0^{1/2} \Gamma P_0^{-1/2}$ , where

$$P_0 = \begin{pmatrix} W_A \\ W_B \end{pmatrix}$$

to yield

$$\dot{\tilde{P}} = \tilde{\Gamma} \tilde{P}, \quad (5.5a)$$

$$\tilde{\Gamma} = \begin{pmatrix} -\tau_A^{-1} & \tilde{\tau}^{-1} \\ \tilde{\tau}^{-1} & -\tau_B^{-1} \end{pmatrix}, \quad (5.5b)$$

$$\tilde{\tau} = \tau_A \sqrt{W_B/W_A} = \tau_B \sqrt{W_A/W_B}.$$

Then one finds

$$P(i|j, \tau) = \tilde{P}(i|j, \tau) = |G_0(i)\rangle \langle G_0(j)| + |G_1(i)\rangle \langle G_1(j)| e^{-k\tau}, \quad i, j = A \text{ or } B \quad (5.6a)$$

where

$$|G_0\rangle = W_A^{1/2} |A\rangle + W_B^{1/2} |B\rangle, \quad (5.6b)$$

$$|G_1\rangle = W_B^{1/2} |A\rangle - W_A^{1/2} |B\rangle, \quad (5.6c)$$

and the bra vectors are of the same form such that  $\langle G_i | G_j \rangle = \delta_{ij}$ . These are the eigenfunctions to use in Eq. (4.4) with  $|P_0\rangle \rightarrow |G_0\rangle$ .

We now introduce a simple secular perturbation for a spin 1/2

$$\mathcal{H} = \bar{\omega} S_x + \lambda(\omega(t) - \bar{\omega}) S_x, \quad (5.7)$$

where

$$\bar{\omega} = \omega_e + \bar{a},$$

and

$$\bar{a} = W_A a_A + W_B a_B,$$

and

$$\omega(t) - \bar{\omega} = a(t) - \bar{a},$$

with

$$\lambda = 1.$$

Then since

$$\langle A | a_i | A \rangle = a_A, \quad (5.8a)$$

$$\langle B | a_i | B \rangle = a_B, \quad (5.8b)$$

we have

$$\langle G_0 | a_i - \bar{a} | G_0 \rangle = 0, \quad (5.9a)$$

$$\langle G_1 | a_i - \bar{a} | G_1 \rangle = (W_B - W_A)(a_A - a_B), \quad (5.9b)$$

$$\langle G_i | a_i - \bar{a} | G_j \rangle = (W_A W_B)^{1/2} (a_A - a_B), \quad i \neq j = 0 \text{ or } 1. \quad (5.9c)$$

Thus we have from Eq. (4.3)

$$\mathcal{G}^*(i\omega) = \sum_{n=1}^{\infty} (i)^{n+1} \frac{W_A W_B (a_A - a_B)^2}{i(\omega - \bar{\omega}) + k} \left[ \frac{(W_B - W_A)(a_A - a_B)}{i(\omega - \bar{\omega}) + k} \right]^{n-1}$$

$$= - \frac{W_A W_B (a_A - a_B)^2}{i(\omega - \bar{\omega}) + k} \left[ 1 - \frac{i(W_B - W_A)(a_A - a_B)}{i(\omega - \bar{\omega}) + k} \right]^{-1}, \quad (5.10)$$

where we have summed the infinite series (without concerning ourselves with the convergence), while from Eq. (4.1) we have

$$I(\omega) \propto \text{Re} \frac{1}{i(\omega - \bar{\omega}) - \mathcal{G}^*(i\omega)}. \quad (5.11)$$

It is quickly seen that this result is just the well-known exact solution (cf. Eq. B1 of Ref. 4) for this simple two-jump model. We note in passing that the higher order-terms in  $\mathcal{G}^*(i\omega)$ , i.e.,  $n > 1$  are nonzero only for  $W_A \neq W_B$ .

(2) Rotational Diffusion, Axially Symmetric Secular  $g$ -Tensor. This is the case of a one-line ESR spectrum broadened mainly by the secular anisotropic  $g$ -tensor term, for which  $g_x = g_y = g_{\perp}$  and  $g_z = g_{\parallel}$ . For this case

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1(\Omega) \quad (5.12)$$

$$\mathcal{H}_0 = \omega_0 S_x \quad (5.13)$$

$$\mathcal{H}_1(\Omega) = \mathcal{D}_{0,0}^2(\Omega) \mathcal{F} S_x \quad (5.14a)$$

$$\mathcal{F} = \frac{2}{3} \hbar^{-1} \beta_e B_0 (g_{\parallel} - g_{\perp}) \quad (5.14b)$$

while the  $\mathcal{D}_{KM}^L(\Omega)$  are the generalized spherical harmonics, which are eigenfunctions of the (axially-symmetric) rotational diffusion equation<sup>4,5</sup>:

$$\Gamma_{\Omega} \mathcal{D}_{KM}^L(\Omega) = R_{\perp} L(L+1) + (R_{\parallel} - R_{\perp}) K^2 \quad (5.15)$$

with rotation diffusion components  $R_x = R_y = R_{\perp}$ ,  $R_z = R_{\parallel}$ . We can introduce conveniently normalized eigenfunctions

$$G_{KM}^L = \sqrt{(2L+1)/8\pi^2} \mathcal{D}_{KM}^L \quad (5.16)$$

and the needed matrix elements  $\langle G_{K_1 M_1}^{L_1} | \mathcal{D}_{KM}^L | G_{K_2 M_2}^{L_2} \rangle$  are well known.<sup>9,10,15</sup> We then obtain from Eq. (4.3):

$$\begin{aligned} \mathcal{G}^*(i\omega) &= \sum_{n=1}^{\infty} \sum_{L_1 \dots L_n}' (i)^{n+1} \langle G_{00}^0 | \mathcal{D}_{00}^2 \mathcal{F} | G_{00}^{L_1} \rangle \langle G_{00}^{L_1} | \frac{\mathcal{D}_{00}^2 \mathcal{F}}{i(\omega - \omega_0) + 6R_{\perp}} | G_{00}^{L_2} \rangle \dots \langle G_{00}^{L_n} | \frac{\mathcal{D}_{00}^2 \mathcal{F}}{i(\omega - \omega_0) + 6R_{\perp}} | G_{00}^0 \rangle \\ &= \sum_{n=1}^{\infty} \sum_{L_2 \dots L_{n-1}}' \frac{(i)^{n+1} \mathcal{F}^{n+1} / 5}{i(\omega - \omega_0) + 6R_{\perp}} \left[ \frac{\sqrt{(2L_2+1)5} \begin{pmatrix} 2 & 2 & L_2 \\ 0 & 0 & 0 \end{pmatrix}^2}{i(\omega - \omega_0) + 6R_{\perp}} \times \frac{\sqrt{(2L_3+1)(2L_3+1)} \begin{pmatrix} L_2 & 2 & L_3 \\ 0 & 0 & 0 \end{pmatrix}^2}{i(\omega - \omega_0) + L_2(L_2+1)R_{\perp}} \right. \\ &\quad \left. \dots \frac{\sqrt{(L_{n-1}+1)5} \begin{pmatrix} L_{n-1} & 2 & 2 \\ 0 & 0 & 0 \end{pmatrix}^2}{i(\omega - \omega_0) + L_{n-1}(L_{n-1}+1)R_{\perp}} \right], \quad (5.17) \end{aligned}$$

where the 3, symbols have been utilized.<sup>15</sup>

In particular, the 2nd, 3rd, and 4th order contributions are

$$\mathcal{G}_2^*(i\omega) = - \frac{\mathcal{F}^2 / 5}{i(\omega - \omega_0) + 6R_{\perp}}, \quad (5.18a)$$

$$\mathcal{G}_3^*(i\omega) = - \frac{i\mathcal{F}^3}{[i(\omega - \omega_0) + 6R_{\perp}]^2} \times \frac{2}{35}, \quad (5.18b)$$

$$\mathcal{G}_4^*(i\omega) = \frac{4}{5 \times 7^2} \frac{\mathcal{F}^4}{[i(\omega - \omega_0) + 6R_{\perp}]^3}$$

$$\times \left[ \frac{1}{i(\omega - \omega_0) + 6R_{\perp}} + \frac{9/5}{i(\omega - \omega_0) + 20R_{\perp}} \right]. \quad (5.18c)$$

This result through  $\mathcal{G}_4$  is equivalent to fourth order in  $\mathcal{F}$  to a solution based on the SLE taken through  $L = 4$  when both results for the lineshapes are expanded in powers of  $\mathcal{F}$ . The TLOC result does appear to be less convenient. Nevertheless, it does allow one to display the general  $n$ th order term, and thus, perhaps, to obtain simplifying features in the analysis. Other, more complex spectral problems, may be analyzed in a similar manner.

VI. THE PTOC METHOD

The TTOC is defined by Eqs. (3.8), (3.10), (3.15), and (3.17). We wish to clarify here the PTOC as used by Freed<sup>4,5</sup> and show it is the natural way to achieve the useful form:

$$\frac{\partial}{\partial t} e_0^{K(t)} = \left[ \frac{\partial}{\partial t} K(t) \right] e_0^{K(t)} = \dot{K}(t) e_0^{K(t)}, \tag{6.1}$$

which was employed there. Thus the PTOC of Freed<sup>4</sup> may be introduced as

$$\begin{aligned} \exp_0 K(t) = & 1 + \sum_{m=1}^{\infty} \lambda^m \int_0^t dt_1 \dots \int_0^{t_{m-1}} dt_m \mathcal{K}_m(t_1, \dots, t_m) + \sum_{m,p=1}^{\infty} \lambda^{m+p} \int_0^t dt_1 \dots \int_0^{t_{m-1}} dt_m \int_0^{t_m} dt_{m+1} \int_0^{t_{m+1}} dt_{m+2} \\ & \dots \int_0^{t_{m+p-1}} dt_{m+p} \mathcal{K}_m(t_1, \dots, t_m) \mathcal{K}_p(t_{m+1} \dots t_{m+p}) + \sum_{m,p,s=1}^{\infty} \lambda^{m+p+s} \int_0^t dt_1 \dots \int_0^{t_{m-1}} dt_m \int_0^{t_m} dt_{m+1} \\ & \dots \int_0^{t_{m+p-1}} dt_{m+p} \int_0^{t_{m+p}} dt_{m+p+1} \dots \int_0^{t_{m+p+s-1}} dt_{m+p+s} \mathcal{K}_m(t_1 \dots t_m) \mathcal{K}_p(t_{m+1} \dots t_{m+p}) \mathcal{K}_s(t_{m+p+1} \dots t_{m+p+s}) + \dots \end{aligned} \tag{6.2}$$

The only differences between Eq. (6.2) and (3.8) are in the upper limits of the time integrals. The  $\mathcal{K}_n$  for  $n \leq 4$  are given in Eqs. (2.14) of Ref. 4 when one utilizes (cf. Ref. 5):

$$K_n(t) \equiv (-i)^n \int_0^t dt_1 \dots \int_0^{t_{n-1}} dt_n \mathcal{K}_n(t_1, t_2, \dots, t_n) \tag{6.3}$$

(One must first reorganize the multiple time integrals to achieve the standard form of Eq. (6.3) as illustrated in Ref. 4). In particular, for

$$\mathcal{K}_1 = \theta_1 = -i \text{Tr}_1 L'(t_1) \rho_1 = 0, \tag{6.4a}$$

one has

$$\mathcal{K}_2 = \theta_2 = -\text{Tr}_1 L'(t_1) L'(t_2) \rho_1, \tag{6.4b}$$

$$\mathcal{K}_3 = \theta_3 = i \text{Tr}_1 L'(t_1) L'(t_2) L'(t_3) \rho_1, \tag{6.4c}$$

$$\begin{aligned} \mathcal{K}_4 = & \theta_4 - \text{Tr}_1 L'(t_1) L'(t_3) \rho_1 \text{Tr}_1 L'(t_2) L'(t_4) \rho_1 \\ & - \text{Tr}_1 L'(t_1) L'(t_4) \rho_1 \text{Tr}_1 L'(t_2) L'(t_3) \rho_1, \end{aligned} \tag{6.4d}$$

with

$$\theta_4 = \text{Tr}_1 L'(t_1) L'(t_2) L'(t_3) L'(t_4) \rho_1$$

$$- \text{Tr}_1 L'(t_1) L'(t_2) \rho_1 \text{Tr}_1 L'(t_3) L'(t_4) \rho_1.$$

Thus, in general, the  $\mathcal{K}_n$  are found to include more terms than the  $\theta_n$  when expanded out. It is now easy to show that

$$\begin{aligned} \frac{\partial}{\partial t} \exp_0 K(t) = & \sum_m \dot{K}_m(t) + \sum_{m,p=1}^{\infty} \dot{K}_m(t) K_p(t) + \sum_{m,p,s=1}^{\infty} \dot{K}_m(t) \int_0^t dt_m \int_0^{t_m} dt_{m+1} \dots \int_0^{t_{m+p-2}} dt_{m+p-1} \int_0^{t_{m+p}} dt_{m+p} \\ & \dots \int_0^{t_{m+p+s-2}} dt_{m+p+s-1} \mathcal{K}_p(t_{m+1} \dots t_{m+p-1}) \mathcal{K}_s(t_{m+p} \dots t_{m+p+s-1}) + \dots = \dot{K}_m(t) \exp_0 K(t), \end{aligned} \tag{6.5}$$

which is just Eq. (6.1).

The PTOC method permits a calculation of the relaxation matrix. We have from Eqs. (2.19) and (A3) and (A4) of Freed,<sup>4</sup> that

$$R = \sum_{n=1}^{\infty} \int_0^{\infty} d\tau_1 \dots \int_0^{\infty} d\tau_{n-1} e^{-iL_s \tau} \mathcal{K}_n(t, t - \tau_1, \dots, t - \sum_{j=1}^{n-1} \tau_j) e^{iL_s t}. \tag{6.6}$$

In particular for a classical lattice described by a stationary-Markov process, the analysis equivalent to that leading to Eq. (3.28) yields

$$R = \sum_{n=1}^{\infty} \int_0^{\infty} d\tau_1 \dots \int_0^{\infty} d\tau_{n-1} \langle P_0 | L' e^{-\tau_1 (iL_s + \Gamma)} L' e^{-\tau_2 (iL_s + \Gamma)} \dots e^{-\tau_{n-1} (iL_s + \Gamma)} L' e^{iL_s \tau} \rangle_{j=1}^{n-1} \tau_j | P_0 \rangle_c + \text{TOTI} \tag{6.7}$$

where the subscript *C* implies the cumulant averaging appropriate for TTOC, i.e., no intermediate states involving  $P_0$ . TOTI are the remaining Terms with Overlapped Time Intervals required for PTOC. One must take spin matrix elements (because of the  $e^{(iL_s + \Gamma) E \tau_j}$  term) before the trivial time integrals of Eq. (6.7) are performed. In particular, taking both spin and lattice "matrix elements" *j* we have

$$\begin{aligned} R_{\alpha\alpha'\beta\beta'} = & \sum_{n=1}^{\infty} \sum_{\substack{m_1, m_2, \\ \dots, m_{n-1}}}^{\infty} \sum_{\substack{\nu_1, \nu_2, \\ \dots, \nu_{n-1}}}^{\infty} (i\lambda)^{n-1} \int_0^{\infty} d\tau_1 \dots \int_0^{\infty} d\tau_{n-1} \langle P_0 | L'_{\alpha\alpha', \nu_1 \nu_1} \exp[-\tau_1 (i\omega_{\nu_1 \nu_1} + E_{m_1})] | G_{m_1} \rangle \\ & \times \langle G_{m_1} | L'_{\nu_1 \nu_1, \nu_2 \nu_2} \exp[-\tau_2 (i\omega_{\nu_2 \nu_2} + E_{m_2})] | G_{m_2} \rangle \dots \langle G_{m_{n-2}} | L'_{\nu_{n-2} \nu_{n-2}, \nu_{n-1} \nu_{n-1}} \exp[-\tau_{n-1} (i\omega_{\nu_{n-1} \nu_{n-1}} + E_{m_{n-1}})] | G_{m_{n-1}} \rangle \\ & \times \langle G_{m_{n-1}} | L'_{\nu_{n-1} \nu_{n-1}, \beta\beta'} \exp \left[ \left( \sum_{j=1}^{n-1} \tau_j \right) (i\omega_{\beta\beta'}) \right] | P_0 \rangle_c + \text{TOTI} \end{aligned} \tag{6.8}$$



$$\begin{aligned}
 &= \sum_n \sum_{m_1} \sum_{\gamma_1 \gamma_1'} \langle P_0 | L'_{\alpha\alpha', \gamma_1 \gamma_1'} / [i(\omega_{\gamma_1 \gamma_1'} - \omega_{\beta\beta'}) + E_{m_1}] | G_{m_1} \rangle \langle G_{m_1} | L'_{\gamma_1 \gamma_1', \gamma_2 \gamma_2'} / [i(\omega_{\gamma_2 \gamma_2'} - \omega_{\beta\beta'}) + E_{m_2}] | G_{m_2} \rangle \\
 &\quad \dots \langle G_{m_{n-2}} | L'_{\gamma_{n-2} \gamma_{n-2}', \gamma_{n-1} \gamma_{n-1}'} / [i(\omega_{\gamma_{n-1} \gamma_{n-1}'} - \omega_{\beta\beta'}) + E_{m_{n-1}}] | G_{m_{n-1}} \rangle \langle G_{m_{n-1}} | L'_{\gamma_{n-1} \gamma_{n-1}', \beta\beta'} | P_0 \rangle_e + \text{TOTI} . \tag{6.9}
 \end{aligned}$$

The TOTI are handled in a similar manner. We illustrate with the contributions to  $K_4$ :

$$\begin{aligned}
 -(\text{TOTI})_4 &= \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \int_0^\infty d\tau_3 [\langle P_0 | L' e^{-i(\tau_1 + \tau_2)(iL_s + \Gamma)} L' e^{iL_s(\tau_1 + \tau_2)} | P_0 \rangle \langle P_0 | L' e^{-i(\tau_2 + \tau_3)(iL_s + \Gamma)} L' e^{iL_s(\tau_2 + \tau_3)} | P_0 \rangle \\
 &\quad + \langle P_0 | L' e^{-i(\tau_1 + \tau_4)(iL_s + \Gamma)} L' e^{iL_s(\tau_1 + \tau_4)} | P_0 \rangle \langle P_0 | L' e^{-i(\tau_2 + \tau_3)(iL_s + \Gamma)} L' e^{iL_s(\tau_2 + \tau_3)} | P_0 \rangle] . \tag{6.10}
 \end{aligned}$$

One must again first take spin matrix elements, and operate with the  $\Gamma$  as already shown in Eqs. (6.8)–(6.9). Then the time integrals again become trivial.

These results for Markov processes are a more convenient version than the expressions given in Ref. 4 for more general processes.

It is important to note that in general

$$\lim_{\omega \rightarrow 0} \mathcal{G}(\omega) \neq R ,$$

where  $\mathcal{G}(0)$  is a zero frequency response, and  $R$  is the long-time limit, unless some motional narrowing limit exists.<sup>7</sup> This is illustrated by the fact that although  $\theta_2 = \mathcal{K}_2$ , we have observed  $\theta_4 \neq \mathcal{K}_4$  and, in general,  $\theta_n \neq \mathcal{K}_n$  for  $n \geq 4$  (with  $\theta_1 = \mathcal{K}_1 = 0$ ). This is why, in general, one may not conveniently obtain  $R$  from  $\mathcal{G}(\omega)$ .

In general, the PTOC method is to be preferred over the TTOC for analyses performed in the time domain. Note that the general solution analogous to Eq. (3.17) is in this case:

$$\dot{\sigma}^*(t) = \dot{K}(t)\sigma^*(t) , \tag{6.11}$$

or

$$\dot{\sigma}(t) = -iL_s\sigma(t) + \dot{K}^\dagger(t)\sigma(t) , \tag{6.11'}$$

with

$$\dot{K}^\dagger(t) \equiv e^{-iL_s t} \dot{K}(t) e^{iL_s t} , \tag{6.11''}$$

which for classical Markov processes may be compared to the SLE Eq. (3.31), which may be rewritten as

$$\dot{\sigma}(t) = -iL_s\sigma(t) + \langle P_0 | (-iL' - \Gamma)\sigma(\Omega, t) | P_0 \rangle , \tag{6.12}$$

with

$$\sigma(t) \equiv \langle P_0 | \sigma(\Omega, t) | P_0 \rangle . \tag{6.12'}$$

While it appears, at first, that Eq. (6.11) is more convenient than Eq. (6.12), it is possible to recast Eq. (6.12) into another form which is more convenient. One uses the technique of expanding  $\sigma(\Omega, t)$  in the eigenfunctions  $G_m(\Omega)$  of  $\Gamma_\Omega$ , cf. Eqs. (3.23)–(3.25):

$$\sigma(\Omega, t) = \sum_m C_m(t) G_m(\Omega) , \tag{6.13}$$

such that the expansion coefficients  $C_m(t)$  are still spin operators.<sup>9–11</sup> Then one obtains for the time evolution of the  $C_m(t)$ :

$$\dot{C}_m(t) = \sum_n \{ -[iL_s + E_m] \delta_{m,n} - i \langle G_m(\Omega) | L' | G_n(\Omega) \rangle \} C_n(t) . \tag{6.14}$$

The bracketed expression in Eq. (6.14) is virtually the same expression required to solve the SLE in the frequency domain [cf. Eq. (3.30) and Refs. 9–11 where here one need only let  $i\omega \rightarrow 0$ ] and the same technique of diagonalizing the ensuing complex (usually) symmetric matrix obtained after spin matrix elements are taken may be employed here as well, in order to obtain the eigenmodes. The long-time limit or  $R$  matrix should be obtainable by performing Van-Vleck-type perturbation theory<sup>9,13,16</sup> on Eq. (6.14) to get the time-evolution of  $C_0(t)$  to  $n$ th order for  $2 \leq n \leq \infty$ . The effects of subsidiary lines etc. [cf. Ref. 4], appear in the coupling of the  $C_m(t)$  for  $m \neq 0$  into the problem. It is, in fact, the difference between the solution of  $C_0(t)$  to  $n$ th order and the contribution of the “subsidiary lines” to the spectrum that leads to the differences between  $R$  and  $\lim_{\omega \rightarrow 0} \mathcal{G}(i\omega)$ .

### VII. SUMMARY

It has been shown that the spin-density matrix equations emerging from the projection operator methods are equivalent to that obtained by the TTOC method. The latter form leads to convenient methods for calculating lineshapes, which, however, are in general deemed not as convenient as the SLE solutions appropriate for lattices described by classical Markov processes. However, it does allow one to study the structure of the important  $n$ th order terms in the actual solution of the spectrum, and this could have important applications.

The PTOC method leads to a different type of solution than the TTOC method. It is the more useful in the time domain. However, again the SLE solutions are more convenient to use, except perhaps in recovering the relaxation matrix in the long-time limit.

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<sup>1</sup>J. Albers and J. M. Deutch, *J. Chem. Phys.* **55**, 2613 (1971).  
<sup>2</sup>J. M. Deutch, in *ESR Relaxation in Liquids*, edited by L. T. Muus and P. W. Atkins (Plenum, New York, 1972), Ch. VII.  
<sup>3</sup>P. N. Argyres and P. L. Kelley, *Phys. Rev.* **134A**, 98 (1964).  
<sup>4</sup>J. H. Freed, *J. Chem. Phys.* **49**, 376 (1968).  
<sup>5</sup>J. H. Freed, in *ESR Relaxation in Liquids*, edited by L. T. Muus and P. W. Atkins (Plenum, New York, 1972), Ch. VIII.  
<sup>6</sup>R. Kubo, *J. Phys. Soc. Japan* **17**, 1100 (1962).  
<sup>7</sup>R. Kubo, *J. Math. Phys.* **4**, 174 (1963).  
<sup>8</sup>R. Kubo, *Adv. Chem. Phys.* **16**, 101 (1969); *J. Phys. Soc. Japan* **26**, Supplement, 1 (1969).  
<sup>9</sup>J. H. Freed, G. V. Bruno, and C. Polnaszek, *J. Phys. Chem.*

- 75, 3385 (1971).
- <sup>10</sup>J. H. Freed, Ref. 5 Ch. XIV.
- <sup>11</sup>J. H. Freed, *Ann. Rev. Phys. Chem.* **23**, 265 (1972).
- <sup>12</sup>Reference 5 pp. 188–190
- <sup>13</sup>C. F. Polnaszek, G. V. Bruno, and J. H. Freed, *J. Chem. Phys.* **58**, 3185 (1973).
- <sup>14</sup>P. Roman, *Advanced Quantum Theory* (Addison-Wesley, Reading, MA, 1965), pp. 392–5.
- <sup>15</sup>A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University, Princeton, 1957).
- <sup>16</sup>E. C. Kemble, *The Fundamental Principles of Quantum Mechanics* (Dover, New York, 1958), p. 394.