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# General Approach to the Line-Shape Problem in Nuclear-Magnetic-Resonance Spectra

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The description of the macroscopic magnetization of an arbitrary sample is first reduced to the calculation of two similar magnetic-moment autocorrelation functions $G(t)$. The nature of the dynamical evolution of the magnetic-moment operator $m(t)$ needed in these correlation functions is then expressed in terms of an infinite set of time-independent orthogonal vectors in a generalized Hilbert space, such that the desired correlations are just the projection of the evolving magnetic-moment operator onto the first of the orthogonal vectors. Equations of motion of the coefficients of the expansion are obtained and formally solved in Laplace-transform form, yielding the transform of $G(t)$ as a ratio of infinite-order determinants. The formalism is related to the procedures of Zwanzig and Mori and, more generally, to the "classical moment problem" of mathematical analysis. Various practical approximations to the rigorous results are examined.

## I. INTRODUCTION

The importance of time-correlation functions in the study of nuclear magnetic resonance (NMR) was first brought out, through a linear-response theory, by Kubo and Tomita.[1,2] Since then, the same approach has been widely applied in nonequilibrium statistical mechanics, providing a rigorous connection between the macroscopic transport coefficients of phenomenological theories and the microscopic molecular properties.[3] Several general techniques, having the necessary feature of treating the many-body dynamical calculation as an initial-value problem, have been devised for the calculation of the autocorrelation functions.[4] The earliest of these is based on an infinite-order perturbation expansion, with selective resummation, developed by van Hove[5] and Prigogine.[6] Later, a mathematically much less formidable approach was devised by Zwanzig,[7] using many-body projection operators to select out only the "relevant" information contained in the full dynamical expressions. More recently, Mori[8] has generalized the projection-operator technique and has obtained an expression for the Laplace transform of an autocorrelation function in the form of a continued fraction. A method related to the latter two is that of Kadanoff and Martin,[9] who approach the problem through the generalized susceptibility.

In the present paper, we apply a new general technique for time-correlation functions to the calculation of the line shape in NMR spectra. This approach, previously employed in the calculation of the van Hove correlation function of classical fluids,[10] is closely related to those of Zwanzig[7] and Mori.[8]

The formalism developed here is quite general, although the determination of the NMR line shapes is of particular interest for the so-called "broad-line" spectra of solids. This is especially so since the discovery by Lowe and Norberg[11] of relatively large oscillations in the $F^{19}$ free-induction-decay (fid) curves from calcium fluoride. These oscillations were clear evidence that the assumption of a Gaussian line shape was not, in general, valid, stimulating further investigations into the detailed NMR line shape.

These latter developments fall generally into one of three categories: (i) direct evaluation of the time autocorrelation function of the transverse magnetization by various methods of approximation; (ii) expansion theorems based on a knowledge of the first few moments of the line shape; and (iii) approximate expressions for the autocorrelation function or the associated memory function based on the general techniques mentioned before.

Direct evaluation of the autocorrelation function has received considerable attention since the original work of Lowe and Norberg.[11] They and others[12–18] have shown that this method is capable of giving good agreement with experiment for short times, i.e., for most of the normally observed fid. However, calcium fluoride fid data taken by Lowe, Bruce, Kessemeier, and Gara[19] for comparatively longer times have shown behavior that is qualitatively different from that predicted by this method.

An alternative procedure is the development of expansion theorems which express the fid curve in terms of known functions incorporating the first few moments of the line shape. The elementary example of this is the moment expansion itself, which—since in practice only the first two even moments are generally known—is quite inadequate for all but very short times. A practical alternative, however, is provided by the Neumann-Gegenbauer expansions of the fid curve.[20] It has been shown[20] that these expansions can be used to

give a very good representation of the short-time behavior of the calcium fluoride fid curves, using only the second and fourth moments. However, in order to predict the long-time behavior using these expansions, a knowledge of more than just these moments is required.

The third procedure is based on equations relating the fid function and its associated memory function.[21-25] These results will be discussed further in the body of the paper.

This work is divided into three main parts. Beginning with the linear-response approximation, the microstate formulas needed for the macroscopic description are systematically developed in Sec. II in a very general fashion. No new results are obtained in Sec. II; the material is presented principally for the sake of completeness. The prediction of the macroscopic magnetization is, in this section, reduced to the calculation of two autocorrelation functions of the same general form. Section III is devoted to a general study of such autocorrelation functions, based on an orthogonal expansion of the dynamical quantity. This approach is seen to be closely related to the methods of Zwanzig[7] and Mori,[8] and, more generally, to the so-called classical moment problem in mathematical analysis,[26] which is intimately connected with the general theory of orthogonal polynomials. Finally, various approximations in the general formalism, which yield practical results suitable for computation, are examined in Sec. IV.

## II. FORMULATION OF PROBLEM

### A. Statistical Description

In a characteristic NMR experiment, a sample of magnetic material is placed in a large static magnetic field $\vec{H}_0$ and allowed to come to equilibrium. Because of the external field, the sample will then possess a constant induced magnetization $\vec{M}_0$. With the equilibrium state having been thus prepared, a weak oscillatory magnetic field $\vec{H}_1(t)$ transverse to $\vec{H}_0$ is switched on, at a time conventionally labeled $t=0$, and the resulting steady-state response of the sample magnetization $\vec{M}(t)$ to the perturbing field $\vec{H}_1(t)$ is determined. More precisely, one measures the line shape of the power absorption from the external field.

In the following paragraphs, we shall follow the outline of this experiment in determining the basic expressions needed for a theoretical analysis of the experimental outcome.

We consider, then, a macroscopic system, which may be a solid, liquid, or gas, made up of a large number $N$ of molecules and contained in the volume $V$ at the temperature $T=(k_B\beta)^{-1}$, where $k_B$ is Boltzmann's constant. For the sake of simplicity, this study will be restricted to systems of identical molecules, each molecule being characterized by a single species of nuclear spin $I$. The spins in the system may be indexed with a subscript $s$; the corresponding magnetic moments are then

$$\vec{\mu}_s=\hbar\gamma\vec{I}_s\,, \tag{2.1}$$

where $\gamma$ is the gyromagnetic ratio.

In principle, the task of determining the macroscopic properties of this system involves a straightforward quantum-mechanical calculation for which just the complete Hamiltonian of the system is needed. For present purposes, it is not necessary to specify this operator beyond its dependence on the external fields, and we write for the total Hamiltonian

$$\mathcal{H}_T(t)=\mathcal{H}+\mathcal{H}'(t)\,,\quad t>0 \tag{2.2}$$

where $\mathcal{H}'(t)$ is the perturbation due to the oscillating field $\vec{H}_1(t)$,

$$\mathcal{H}'(t)=-\textstyle\sum_s\vec{\mu}_s\cdot\vec{H}_1(t)\,, \tag{2.3}$$

and $\mathcal{H}$ is the equilibrium Hamiltonian. This latter operator in turn is written

$$\mathcal{H}=\mathcal{H}_0+\mathcal{H}_z\,, \tag{2.4}$$

where

$$\mathcal{H}_z=-\textstyle\sum_s\vec{\mu}_s\cdot\vec{H}_0 \tag{2.5}$$

is the Zeeman energy, and $\mathcal{H}_0$ is the Hamiltonian of the completely isolated system. The operator $\mathcal{H}_0$, containing contributions from both the spin and molecular degrees of freedom, can for the moment remain unspecified. We shall later need to make a general assumption about the invariance properties of $\mathcal{H}_0$, but since specific calculations will not be made we will not need an explicit form of this operator.

To obtain the measured properties of the system, one must then solve the time-dependent Schrödinger equation for the wave function $\psi(t)$ of the system at all times. This equation, however, is of first order in time, so that a final specification of $\psi(t)$ (assuming a solution could be found) requires a knowledge of the initial wave function $\psi(0)$. Since this information is, in general, not available—all one knows is that the system has been prepared in a state of macroscopic equilibrium—it is at this point that a statistical description must enter. For this, one needs the statistical density operator $\rho(t)$, in terms of which the average behavior of the observable which corresponds to the Hermitian operator $A$ is given by

$$\langle A(t)\rangle=\mathrm{Tr}\{\rho(t)A\}\,. \tag{2.6}$$

The density operator also satisfies an equation that

is of first order in time, namely, the quantum-mechanical Liouville equation

$$i\hbar \frac{\partial \rho(t)}{\partial t} = [\mathcal{H} + \mathcal{H}'(t), \rho(t)] , \tag{2.7}$$

which, needless to say, is no easier to solve than the Schrödinger equation from which it is obtained. But the initial value $\rho(0)$ is now a known quantity. Since the sample was prepared in thermal equilibrium at the temperature $T$, $\rho(0)$ is just the canonical density operator

$$\rho(0) = (1/Z)\, e^{-\beta \mathcal{H}} , \tag{2.8}$$

$$Z = \mathrm{Tr}\, e^{-\beta \mathcal{H}} , \tag{2.9}$$

where $\mathcal{H}$ is the equilibrium Hamiltonian, Eq. (2.4). That is, a statistical assumption is made only for the initial state of the system; its dynamical evolution is still governed by the total Hamiltonian $\mathcal{H}_T(t)$.

### B. Linear Response and Magnetization

An explicit solution of Eqs. (2.7) and (2.8) for the dynamical evolution of the density operator $\rho(t)$ is not possible. However, a formal solution, that is, one which leaves the dynamical calculations implicit and still to be performed, can be easily obtained. To do so, we rewrite (2.7) in the form

$$i\hbar \frac{\partial}{\partial t} \{ e^{it\mathcal{H}/\hbar} \rho(t)\, e^{-it\mathcal{H}/\hbar} \} = e^{it\mathcal{H}/\hbar} [\mathcal{H}'(t), \rho(t)]\, e^{-it\mathcal{H}/\hbar} , \tag{2.10}$$

and integrate both sides from 0 to $t$. After transposing the exponential operators, we arrive at an integral equation for $\rho(t)$, namely,

$$\rho(t) = \rho(0) - (i/\hbar) \int_0^t dt'\, e^{i(t'-t)\mathcal{H}/\hbar} \times [\mathcal{H}'(t'), \rho(t')]\, e^{-i(t'-t)\mathcal{H}/\hbar} , \tag{2.11}$$

or, with the explicit form of $\mathcal{H}'(t)$ from (2.3)

$$\rho(t) = \rho(0) + (i/\hbar) \int_0^t dt'\, e^{i(t'-t)\mathcal{H}/\hbar} \times [\vec{\mathrm{H}}_1(t') \cdot \vec{\mu}, \rho(t')]\, e^{-i(t'-t)\mathcal{H}/\hbar} , \tag{2.12}$$

where we have put, for brevity,

$$\vec{\mu} \equiv \textstyle\sum_s \vec{\mu}_s . \tag{2.13}$$

Equation (2.12) can be formally solved by iteration, producing a functional expansion of $\rho(t)$ in powers of $\vec{\mathrm{H}}_1(t)$,

$$\rho(t) = \rho(0) + (i/\hbar) \int_0^t dt' [\vec{\mathrm{H}}_1(t') \cdot \vec{\mu}(t'-t), \rho(0)] + (i/\hbar)^2 \int_0^t dt' \int_0^{t'} dt'' [\vec{\mathrm{H}}_1(t') \cdot \vec{\mu}(t'-t), [\vec{\mathrm{H}}_1(t'') \cdot \vec{\mu}(t''-t), \rho(0)]] + \cdots . \tag{2.14}$$

In obtaining (2.14), we have used the fact that $e^{it\mathcal{H}/\hbar}$ commutes with $\rho(0)$ and have introduced the Heisenberg operator

$$\vec{\mu}(t) = e^{it\mathcal{H}/\hbar} \vec{\mu}\, e^{-it\mathcal{H}/\hbar} , \tag{2.15}$$

which describes the time evolution of the spin operators. One now uses the presumed smallness of $\vec{\mathrm{H}}_1(t)$ to justify neglect of all terms in (2.14) beyond the linear one, so that (2.14) is approximated by

$$\rho(t) = \rho(0) + (i/\hbar) \int_0^t dt' [\vec{\mathrm{H}}_1(t') \cdot \vec{\mu}(t'-t), \rho(0)] . \tag{2.16}$$

This is the linear-response approximation,[1] and its use, as is well known, will restrict the ensuing formalism to situations far removed from saturation.

The central quantity we wish to determine is the net sample magnetization $\vec{\mathrm{M}}(t)$, which, in terms of an ensemble average, is given by

$$\vec{\mathrm{M}}(t) = (1/V)\, \mathrm{Tr}\{\rho(t) \vec{\mu}\} . \tag{2.17}$$

In using the linear approximation (2.16), one assumes the response is strictly proportional to the perturbing field

$$\vec{\mathrm{M}}(t) = \vec{\mathrm{M}}_0 + (i/\hbar V) \int_0^t dt'\, \mathrm{Tr}\{ [\vec{\mathrm{H}}_1(t') \cdot \vec{\mu}(t'-t), \rho(0)] \vec{\mu} \} , \tag{2.18}$$

where

$$\vec{\mathrm{M}}_0 \equiv \vec{\mathrm{M}}(0) = (1/V)\, \mathrm{Tr}\{\rho(0) \vec{\mu}\} . \tag{2.19}$$

As noted, this assumption breaks down near saturation.

Because the trace of a product of operators is invariant to a cyclic permutation of the operators, (2.18) may be rewritten in the form

$$\vec{\mathrm{M}}(t) = \vec{\mathrm{M}}_0 - (i/\hbar V) \int_0^t dt' \langle [\vec{\mathrm{H}}_1(t') \cdot \vec{\mu}(0), \vec{\mu}(t-t')] \rangle , \tag{2.20}$$

or, in component notation and after a change in integration variable from $t-t'$ to $t'$,

$$M_a(t) = M_{0a} - (i/\hbar V) \textstyle\sum_b \int_0^t dt'\, H_{1b}(t-t') \langle [\mu_b(0), \mu_a(t')] \rangle . \tag{2.21}$$

Alternatively, the commutator in (2.18) may be formally eliminated using a technique due to Kubo.[27] Using (2.8), we have

$$[\mu_b(t), \rho(0)] = \rho(0) \{ e^{\beta \mathcal{H}} \mu_b(t)\, e^{-\beta \mathcal{H}} - \mu_b(t) \} = \rho(0) \int_0^\beta d\lambda \frac{d}{d\lambda} \{ e^{\lambda \mathcal{H}} \mu_b(t)\, e^{-\lambda \mathcal{H}} \}$$

$$= -i\hbar\rho(0)\frac{d}{dt}\int_0^\beta d\lambda\, e^{\lambda\mathcal{H}}\mu_b(t)\,e^{-\lambda\mathcal{H}}$$

$$= -i\hbar\beta\rho(0)\frac{d\bar{\mu}_b(t)}{dt}\,, \qquad (2.22)$$

where the equivalence of $d/d\lambda$ and $-i\hbar(d/dt)$ follows from the similar role played by $\lambda$ and $it/\hbar$ in these expressions [cf. (2.15)]. The last equality in (2.22) defines the Kubo transform $\bar{\mu}_b(t)$ of $\mu_b(t)$. In general,

$$\bar{A} = (1/\beta)\int_0^\beta d\lambda\, e^{\lambda\mathcal{H}}Ae^{-\lambda\mathcal{H}} \qquad (2.23)$$

defines the Kubo transform of the operator $A$. If $A$ commutes with $\mathcal{H}$, then obviously $\bar{A}=A$. This equality also holds approximately in the noncommuting case at high temperatures. Using (2.22) in (2.18) we get for the magnetization of the sample

$$M_a(t) = M_{0a} - \frac{\beta}{V}\sum_b\int_0^t dt'\,H_{1b}(t-t')\,\frac{d}{dt'}\langle\bar{\mu}_b(0)\,\mu_a(t')\rangle\,. \qquad (2.24)$$

Thus, we find that in the linear-response approximation the calculation of the time-dependent magnetization reduces to a knowledge of the correlation tensor $\langle\bar{\mu}_b(0)\,\mu_a(t)\rangle$.

### C. Relaxation and Response Functions

The function $\langle\bar{\mu}_b(0)\mu_a(t)\rangle$ describes the extent to which the value of $\mu_a$ at time $t$ is connected to the initial value of $\bar{\mu}_b$. For very large separations in time, it is expected on physical grounds that this connection should be negligible; that is,

$$\lim_{t\to\infty}\langle\bar{\mu}_b(0)\mu_a(t)\rangle = \langle\bar{\mu}_b(0)\rangle\langle\mu_a(t)\rangle$$

$$= \langle\mu_b\rangle\langle\mu_a\rangle$$

$$= V^2M_{0b}M_{0a}\,. \qquad (2.25)$$

Define now

$$F_{ab}(t) \equiv (1/V)\langle\bar{\mu}_b(0)\mu_a(t)\rangle - (1/V)\langle\mu_b\rangle\langle\mu_a\rangle$$

$$= (1/V)\langle\bar{m}_b(0)m_a(t)\rangle\,, \qquad (2.26)$$

where $m_a$ is a magnetic-moment fluctuation

$$m_a \equiv \mu_a - \langle\mu_a\rangle\,. \qquad (2.27)$$

Evidently, $F_{ab}(t)$, called the relaxation tensor, becomes negligible with increasing time. It describes the relaxation of the spins from an initial nonequilibrium state.

With the further definition

$$R_{ab}(t) \equiv -\beta\frac{d}{dt}F_{ab}(t)\,, \qquad (2.28)$$

(2.24) may be written

$$M_a(t) = M_{0a} + \sum_b\int_0^t dt'\,R_{ab}(t')H_{1b}(t-t')\,. \qquad (2.29)$$

The physical meaning of $R_{ab}(t)$ may be inferred from this equation. The magnetization $M_a(t)$ at time $t$ responds not only to the perturbing field at that time, but also, through the spin interactions, to values of the field at earlier times which left their effect in the microscopic spin states. This indirect response is described by $R_{ab}(t-t')$, known as the response tensor, which gives in effect the weight to be assigned to the field at $t'$ in computing the magnetization at $t$. Like $F_{ab}(t)$, the response tensor will become negligible for large separations in time.

### D. Time-Correlation Functions $G_{ab}(t)$ and Related Functions

In this section, we will establish several general properties of the relaxation tensor

$$F_{ab}(t) = (1/\beta V)\int_0^\beta d\lambda\,\mathrm{Tr}\{\rho(0)e^{\lambda\mathcal{H}}m_be^{-\lambda\mathcal{H}}\,e^{it\mathcal{H}/\hbar}m_ae^{-it\mathcal{H}/\hbar}\} \qquad (2.30)$$

By cyclic permutation of the operators under the trace and a change in integration variable from $\lambda$ to $\beta-\lambda$, the definition yields

$$F_{ab}(t) = (1/\beta V)\int_0^\beta d\lambda\,\mathrm{Tr}\{\rho(0)e^{(\beta-\lambda)\mathcal{H}}m_ae^{-(\beta-\lambda)\mathcal{H}} \times e^{-it\mathcal{H}/\hbar}m_b\,e^{it\mathcal{H}/\hbar}\}$$

$$= (1/\beta V)\int_0^\beta d\lambda\,\mathrm{Tr}\{\rho(0)e^{\lambda\mathcal{H}}m_a\,e^{-\lambda\mathcal{H}}m_b(-t)\}$$

$$= (1/V)\langle\bar{m}_a(0)m_b(-t)\rangle = F_{ba}(-t)\,. \qquad (2.31)$$

The diagonal elements are thus even in time. Furthermore, by choosing eigenfunctions of $\mathcal{H}$ to write out the trace explicitly, we get

$$F_{ab}(t) = \frac{1}{\beta VZ}\int_0^\beta d\lambda\sum_{n,k}e^{-\beta E_n}\,e^{\lambda(E_n-E_k)} \times e^{-it(E_n-E_k)/\hbar}\langle n|m_b|k\rangle\langle k|m_a|n\rangle$$

$$= \frac{1}{\beta VZ}\int_0^\beta d\lambda\sum_{n,k}\{e^{-\beta E_k}\,e^{(\beta-\lambda)(E_k-E_n)} \times e^{-it(E_k-E_n)/\hbar}\langle k|m_b|n\rangle\langle n|m_a|k\rangle\}^*$$

$$= F^*_{ab}(t)\,, \qquad (2.32)$$

where the asterisk denotes complex conjugate. Thus, all the elements of $F_{ab}(t)$ are real, as was to be expected since they are measurable quantities.

Additional symmetries of $F_{ab}(t)$ can be found by

considering rotations in space generated by the unitary operator

$$U(\hat{n}\theta)=e^{-i\hat{n}\cdot\vec{J}\theta/\hbar} \quad , \tag{2.33}$$

where $\vec{J}$ is the total angular momentum of the system

$$\vec{J}=-\sum_j \vec{r}_j\times i\hbar\nabla_j+\sum_s \hbar\vec{I}_s \quad . \tag{2.34}$$

Here $j$ runs over the particles that make up the system. In (2.33), $\hat{n}$ is the axis of rotation and $\theta$ is the angle turned. The necessary requirement for establishing the symmetries is that $\mathcal{H}=\mathcal{H}_0+\mathcal{H}_z$ be invariant under rotation

$$U(\hat{n}\theta)\mathcal{H}U(\hat{n}\theta)^{-1}=\mathcal{H} \quad . \tag{2.35}$$

We shall assume that $\mathcal{H}_0$ contains molecular potentials dependent only on interparticle separations and spin interactions such as dipolar coupling, so that (2.35) is always satisfied by $\mathcal{H}_0$. The Zeeman Hamiltonian is invariant to rotations about the direction of $\vec{H}_0$, which we take to be in the $z$ direction. Therefore, for a $\frac{1}{2}\pi$ rotation about the $z$ axis, we get

$$F_{ab}(t)=\frac{1}{V}\left\langle U\left(\hat{k}\,\frac{\pi}{2}\right)^{-1}U\left(\hat{k}\,\frac{\pi}{2}\right)\bar{m}_b(0)m_a(t)\right\rangle$$

$$=\frac{1}{V}\langle\bar{m}_b'(0)m_a'(t)\rangle \quad , \tag{2.36}$$

with

$$U(\hat{k}\tfrac{1}{2}\pi)m_a\,U(\hat{k}\tfrac{1}{2}\pi)^{-1}\equiv m_a' \quad . \tag{2.37}$$

In general, a rotation of $\theta$ about the $z$ axis produces

$$\begin{aligned} U(\hat{k}\theta)m_x\,U(\hat{k}\theta)^{-1}&=m_x\cos\theta+m_y\sin\theta \quad ,\\ U(\hat{k}\theta)m_y\,U(\hat{k}\theta)^{-1}&=-m_x\sin\theta+m_y\cos\theta \quad ,\\ U(\hat{k}\theta)m_z\,U(\hat{k}\theta)^{-1}&=m_z \quad , \end{aligned} \tag{2.38}$$

so that in the present case we have

$$m_x'=m_y \quad , \quad m_y'=-m_x, \quad m_z'=m_z \quad , \tag{2.39}$$

and consequently (2.36) yields

$$\begin{aligned} &F_{xx}(t)=F_{yy}(t), \quad F_{xy}(t)=-F_{yx}(t) \quad ,\\ &F_{xz}(t)=F_{yz}(t)=F_{zx}(t)=F_{zy}(t)=0 \quad . \end{aligned} \tag{2.40}$$

Therefore, there are only three distinct elements of $F_{ab}(t)$ that must be determined: $F_{xx}$, $F_{xy}$, and $F_{zz}$.

Similarly, a rotation of $\pi$ about the $y$ axis combined with a reversal of the direction of $\vec{H}_0$ to accommodate the Zeeman term will leave the Hamiltonian unchanged. Use of these operations then produces the result

$$\begin{aligned} F_{xx}(t;H_0)&=F_{xx}(t;-H_0) \quad ,\\ F_{xy}(t;H_0)&=-F_{xy}(t;-H_0) \quad ,\\ F_{zz}(t;H_0)&=F_{zz}(t;-H_0) \quad , \end{aligned} \tag{2.41}$$

where the reversal of $\vec{H}_0$ is explicitly indicated.

It will be convenient to collect these results for later reference. Combining (2.31), (2.32), (2.40), and (2.41), we have

$$\begin{aligned} F_{xx}(t)&=F_{xx}(-t)=F_{xx}^*(t) \quad ,\\ F_{xx}(t;H_0)&=F_{xx}(t;-H_0) \quad , \end{aligned} \tag{2.42a}$$

$$\begin{aligned} F_{xy}(t)&=-F_{xy}(-t)=F_{xy}^*(t) \quad ,\\ F_{xy}(t;H_0)&=-F_{xy}(t;-H_0) \quad , \end{aligned} \tag{2.42b}$$

$$\begin{aligned} F_{zz}(t)&=F_{zz}(-t)=F_{zz}^*(t) \quad ,\\ F_{zz}(t;H_0)&=F_{zz}(t;-H_0) \quad . \end{aligned} \tag{2.42c}$$

Actually, we shall not try to evaluate these three functions directly. Instead, it will suffice to determine two somewhat simpler correlation functions, as will now be shown. The Fourier transform of $F_{ab}(t)$ is

$$\tilde{F}_{ab}(\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}dt\,e^{-i\omega t}F_{ab}(t)$$

$$=\frac{1}{\beta}\int_0^{\beta}d\lambda\,\frac{1}{2\pi}\int_{-\infty}^{\infty}dt\,e^{-i\omega t}\,\frac{1}{V}\langle m_b(0)m_a(t+i\hbar\lambda)\rangle$$

$$=\frac{1}{\beta}\int_0^{\beta}d\lambda\,e^{-\hbar\omega\lambda}\,\frac{1}{2\pi}\int_{-\infty}^{\infty}dt\,e^{-i\omega(t+i\hbar\lambda)}\,\frac{1}{V}\langle m_b(0)m_a(t+i\hbar\lambda)\rangle$$

$$=\frac{1}{\beta}\int_0^{\beta}d\lambda\,e^{-\hbar\omega\lambda}\,\frac{1}{2\pi}\int_{-\infty}^{\infty}dt\,e^{-i\omega t}\,\frac{1}{V}\langle m_b(0)m_a(t)\rangle \quad . \tag{2.43}$$

The last equality in (2.43) is obtained by integrating the analytic function $e^{i\omega z}\langle m_b(0)m_a(z)\rangle$ around the contour shown in Fig. 1 and applying the residue theorem. The $\lambda$ integration in (2.43) may now be carried out with the result

$$\tilde{F}_{ab}(\omega)=\frac{1-e^{-\beta\hbar\omega}}{\beta\hbar\omega}\,\frac{1}{2\pi}\int_{-\infty}^{\infty}dt\,e^{-i\omega t}\,\frac{1}{V}\langle m_b(0)m_a(t)\rangle \quad . \tag{2.44}$$

Because of (2.31), it follows that

$$\tilde{F}_{ab}(\omega)=\tilde{F}_{ba}(-\omega) \quad , \tag{2.45}$$

so that, after the appropriate changes in (2.44), we have alternatively

$$\tilde{F}_{ab}(\omega)=\frac{e^{\beta\hbar\omega}-1}{\beta\hbar\omega}\,\frac{1}{2\pi}\int_{-\infty}^{\infty}dt\,e^{-i\omega t}\,\frac{1}{V}\langle m_a(t)m_b(0)\rangle \quad . \tag{2.46}$$

These results may be combined by first writing them in the form

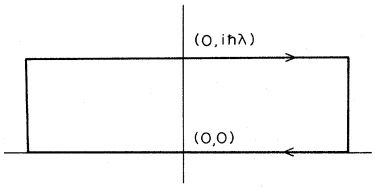


FIG. 1. Contour for the integral in Eq. (2.43).

$$e^{(1/2)\beta\hbar\omega}\tilde{F}_{ab}(\omega)=\frac{2\sinh\frac{1}{2}\beta\hbar\omega}{\beta\hbar\omega}\times\frac{1}{2\pi}\int_{-\infty}^{\infty}dt\,e^{-i\omega t}\frac{1}{V}\langle m_b(0)m_a(t)\rangle\ , \tag{2.47}$$

$$e^{(-1/2)\beta\hbar\omega}\tilde{F}_{ab}(\omega)=\frac{2\sinh\frac{1}{2}\beta\hbar\omega}{\beta\hbar\omega}\times\frac{1}{2\pi}\int_{-\infty}^{\infty}dt\,e^{-i\omega t}\frac{1}{V}\langle m_a(t)m_b(0)\rangle\ , \tag{2.48}$$

and then adding the two equations. The result is

$$\tilde{F}_{ab}(\omega)=\frac{2}{\beta\hbar\omega}\tanh(\tfrac{1}{2}\beta\hbar\omega)\frac{1}{2\pi}\int_{-\infty}^{\infty}dt\,e^{-i\omega t}\times\frac{1}{2V}\langle m_b(0)m_a(t)+m_a(t)m_b(0)\rangle\ . \tag{2.49}$$

Define now the (unsymmetrized) time-correlation function of the spins:

$$G_{ab}(t)\equiv(1/V)\langle m_b(0)m_a(t)\rangle\ . \tag{2.50}$$

Then we have

$$(1/V)\langle m_a(t)m_b(0)\rangle=(1/V)\langle m_a(0)m_b(-t)\rangle=G_{ba}(-t)\ , \tag{2.51}$$

and so (2.49) becomes

$$\tilde{F}_{ab}(\omega)=(2/\beta\hbar\omega)\tanh(\tfrac{1}{2}\beta\hbar\omega)\tfrac{1}{2}[\tilde{G}_{ab}(\omega)+\tilde{G}_{ba}(-\omega)]\ . \tag{2.52}$$

Now $G_{ab}(t)$ will have the same symmetries as $F_{ab}(t)$ under rotations, Eqs. (2.40). Specifically, the $xy$ component will yield

$$\tilde{G}_{yx}(\omega)=-\tilde{G}_{xy}(\omega)\ . \tag{2.53}$$

With this addition, the equations for $\tilde{F}_{xx}$, $\tilde{F}_{xy}$, and $\tilde{F}_{zz}$ from (2.52) are, explicitly,

$$\tilde{F}_{xx}(\omega)=\tfrac{1}{2}B(\omega)[\tilde{G}_{xx}(\omega)+\tilde{G}_{xx}(-\omega)]\ , \tag{2.54a}$$

$$\tilde{F}_{xy}(\omega)=\tfrac{1}{2}B(\omega)[\tilde{G}_{xy}(\omega)-\tilde{G}_{xy}(-\omega)]\ , \tag{2.54b}$$

$$\tilde{F}_{zz}(\omega)=\tfrac{1}{2}B(\omega)[\tilde{G}_{zz}(\omega)+\tilde{G}_{zz}(-\omega)]\ , \tag{2.54c}$$

where

$$B(\omega)\equiv(2/\beta\hbar\omega)\tanh\tfrac{1}{2}\beta\hbar\omega\ . \tag{2.55}$$

If the frequencies of interest [i.e., where $\tilde{G}(\omega)$ is not negligible] are such that

$$\hbar\omega\ll kT\ , \tag{2.56}$$

then

$$B(\omega)\approx 1 \tag{2.57}$$

and the Eqs. (2.54) may be simplified to this extent. This condition holds in most NMR experiments; the simplification contributed by (2.57), however, is not very helpful.

Finally, we introduce the combinations

$$m_+\equiv m_x+im_y,\quad m_-\equiv m_x-im_y\ , \tag{2.58}$$

and define the correlation function

$$\begin{aligned}G_{-+}(t)&\equiv(1/V)\langle m_+(0)m_-(t)\rangle\\&=G_{xx}(t)+G_{yy}(t)+i[G_{xy}(t)-G_{yx}(t)]\\&=2[G_{xx}(t)+iG_{xy}(t)]\ ,\end{aligned} \tag{2.59}$$

and similarly

$$G_{+-}(t)=2[G_{xx}(t)-iG_{xy}(t)]\ . \tag{2.60}$$

But from Eqs. (2.41) (with $G$ replacing $F$), it follows that

$$G_{+-}(t;H_0)=G_{-+}(t;-H_0)\ , \tag{2.61}$$

so that we have

$$\begin{aligned}G_{xx}(t)&=\tfrac{1}{4}[G_{-+}(t;H_0)+G_{-+}(t;-H_0)]\ ,\\G_{xy}(t)&=-\tfrac{1}{4}i[G_{-+}(t;H_0)-G_{-+}(t;-H_0)]\ .\end{aligned} \tag{2.62}$$

Thus, a knowledge of $G_{-+}$ is sufficient to determine both $G_{xx}$ and $G_{xy}$. Additional symmetries of the various correlation functions $G$ and their transforms can readily be obtained. In the following, however, we shall explicitly need only one of these. Writing out the trace as in (2.32), we find that

$$G_{ab}(-t)=G^*_{ba}(t)\ , \tag{2.63}$$

from which it follows that

$$G_{-+}(-t)=G^*_{-+}(t)\ . \tag{2.64}$$

Let us summarize the results of Sec. II. We began with the general problem of determining the nine components of the relaxation tensor $F_{ab}(t)$ and found that, when $\vec{H}_0$ was in the $z$ direction, it was only necessary to evaluate three of these, $F_{xx}(t)$, $F_{xy}(t)$, and $F_{zz}(t)$, provided that $\mathcal{H}_0$ was invariant to spatial rotation. It was then shown that the corresponding three components of the simpler correlation tensor $G_{ab}(t)$ gave the desired information. And finally, we now find that we need to determine just the two cor-

relation functions

$$G_{-+}(t) = (1/V)\langle m_+(0)m_-(t)\rangle = (1/V)\langle m_-^*(0)m_-(t)\rangle \tag{2.65}$$

and

$$G_{zz}(t) = (1/V)\langle m_z(0)m_z(t)\rangle = (1/V)\langle m_z^*(0)m_z(t)\rangle , \tag{2.66}$$

in order to completely solve the original task of determining $F_{ab}(t)$.

Equations (2.65) and (2.66) have been written as shown to bring out the fact that they are both autocorrelation functions of the same general form. In Sec. III, we present a general technique for the calculation of autocorrelation functions of this form.

## III. EVALUATION OF TIME-AUTOCORRELATION FUNCTIONS

### A. Liouville Operator

In Sec. II, we have shown how the calculation of the macroscopic magnetization of a sample reduces, in the linear-response approximation, to the calculation of two time-autocorrelation functions of the general form

$$G(t) = (1/V)\langle m^*(0)m(t)\rangle , \tag{3.1}$$

where

$$m(t) = e^{it\mathcal{H}/\hbar} m e^{-it\mathcal{H}/\hbar} \tag{3.2}$$

and

$$\langle m\rangle = 0 . \tag{3.3}$$

Here $m$ can be either $m_-$ or $m_z$ and we shall use this undifferentiated notation throughout Sec. III.

There are two distinct problems in the calculation of $G(t)$. First, one must determine explicitly the time evolution of the fluctuation $m(t)$ from some given initial state, expressed formally by (3.2). This is a many-body dynamical calculation which does not involve statistics. And second, one must then perform a thermal average over all possible initial states. This statistical averaging is done over an equilibrium ensemble.

Of these stages, the first is the more difficult. In the following paragraphs, we will show how the dynamical problem of evaluating $m(t)$ may be reduced to the statistical one of evaluating thermal averages. This, of course, is also achieved with the straightforward moment expansion, with only modest progress towards determining $G(t)$ for all times, since, in practice, only the first few moments can actually be evaluated. We shall see that, indeed, the moment expansion is closely related to the present method, but that the practical gain that can be obtained from a knowledge of the first few moments will be much greater.

As noted, the dynamical problem is contained in the calculation of $m(t)$, whose equation of motion is, from (3.2),

$$\frac{\partial m(t)}{\partial t} = \frac{i}{\hbar}[\mathcal{H}, m(t)] . \tag{3.4}$$

Define now the Liouville operator

$$L \equiv (1/\hbar)[\mathcal{H}, \ ] , \tag{3.5}$$

so that (3.4) becomes

$$\frac{\partial m(t)}{\partial t} = iLm(t) , \tag{3.6}$$

which has the formal solution

$$m(t) = e^{itL} m . \tag{3.7}$$

That (3.2) and (3.7) are identical can easily be verified by expansion of the exponential operators in both cases, and term by term comparison of the resulting series expansions.

Note that $L$ is a linear operator that operates on other operators, rather than directly on quantum states. It is useful, particularly for visualization, to introduce a Hilbert space of operators with the inner product

$$(A|B) \equiv \langle A^\dagger B\rangle \tag{3.8}$$

for arbitrary operators $A$ and $B$, where $A^\dagger$ is the Hermitian conjugate of $A$, and the angular brackets denote an equilibrium thermal average, as before. This definition of inner product satisfies the usual requirements

$$(A|B) = (B|A)^* , \tag{3.9}$$

$$(a_1A_1 + a_2A_2|B) = a_1^*(A_1|B) + a_2^*(A_2|B) , \tag{3.10}$$

$$(A|A) \geq 0 , \tag{3.11}$$

where $a_1$ and $a_2$ are arbitrary scalars and the equality in (3.11) holds only if $A$ is the null operator. In this scheme, we will be able to discuss an operator $A$ more graphically by referring to $|A)$ as a vector with a real positive norm $(A|A)$.

With the inner product (3.8), $L$ is a Hermitian operator in the Hilbert space of operators, for we now have

$$(A|L|B) = \langle A^\dagger LB\rangle = (1/\hbar)\langle A^\dagger[\mathcal{H}, B]\rangle = (1/\hbar)\langle[\mathcal{H}, A]^\dagger B\rangle$$
$$= \langle (LA)^\dagger B\rangle = (B|L|A)^* , \tag{3.12}$$

as required. Furthermore, in this notation, the desired correlation function is

$$G(t) = (1/V)(m(0)|m(t)) \tag{3.13}$$

$$= (1/V)(m(0)|e^{itL}|m(0)) , \tag{3.14}$$

and we see that what we are seeking is, in geometric terms, the projection of the rotating vector $|m(t))$ onto the stationary vector $|m(0))$, as a function of time.

### B. Moment Expansion

The moment expansion of a time-correlation function offers one possible approach to its calculation. By expanding the exponential operator in (3.14), we get

$$G(t)=G(0)\sum_{n=0}^{\infty}\frac{(it)^n}{n!}M_n\,, \tag{3.15}$$

where

$$G(0)=(1/V)(m(0)\,|\,m(0))\tag{3.16}$$

and

$$M_n=\frac{(m(0)\,|\,L^n\,|\,m(0))}{(m(0)\,|\,m(0))}\,. \tag{3.17}$$

The quantity $M_n$ appearing in (3.15) and defined in (3.17) is just the $n$th moment of the spectral function

$$S(\omega)\equiv\tilde{G}(\omega)/G(0) \tag{3.18}$$

$$=\frac{1}{2\pi G(0)}\int_{-\infty}^{\infty}dt\,e^{-i\omega t}G(t)\,. \tag{3.19}$$

This is easily seen by writing the inverse of (3.19)

$$G(t)/G(0)=\int_{-\infty}^{\infty}d\omega\,e^{i\omega t}S(\omega)\,, \tag{3.20}$$

and expanding $e^{i\omega t}$ in the integrand. We find by comparison with (3.15) that

$$\langle\omega^n\rangle\equiv\int_{-\infty}^{\infty}d\omega\,\omega^n S(\omega)=M_n\,. \tag{3.21}$$

Actually, these are not the moments that are generally of interest in NMR calculations. Instead, since $S(\omega)$ is, in general, symmetrical about a nonzero frequency $\omega_0$, the central moments $\langle(\omega-\omega_0)^n\rangle$ are more directly useful. This feature will emerge naturally from the following analysis.

The difficulty with the moment expansion (3.15) is that it is only slowly convergent, while the moments themselves become rapidly more difficult to evaluate. In practice, therefore, the straightforward moment expansion is suitable only for calculating $G(t)$ for very short times $t$. A variation of this approach, however, offers more general promise.

### C. Orthogonal Expansion of $|m(t))$

Let us return to the dynamical problem of evaluating

$$|m(t))=e^{itL}|m(0))\,. \tag{3.22}$$

As noted above, one could simply expand the exponential operator, producing a series expansion for $m(t)$ with an explicit time dependence:

$$|m(t))=\sum_{j=0}^{\infty}\frac{(it)^j}{j!}\,|L^j m(0))\,. \tag{3.23}$$

This expansion leads directly to the moment expansion for $G(t)$, which is not satisfactory. However, (3.23) provides a complete set of basis functions $|L^j m(0))$ for the representation of $|m(t))$. Since we wish to compute the projection of $|m(t))$ onto the first, or $j=0$, member of this set, the creation of an orthogonal set of basis functions from the given set $|L^j m(0))$ seems a natural approach. We use the Schmidt orthogonalization process and define

$$\begin{aligned}|0)&=|m(0))\,,\\ |j)&=L^j|m(0))-\sum_{k=0}^{j-1}\frac{(k\,|L^j\,|m(0))}{(k\,|k)}\,|k)\,.\end{aligned} \tag{3.24}$$

Then $|m(t))$ may be represented in this basis set as

$$|m(t))=\sum_{j=0}^{\infty}A_j(t)\,|j)\,, \tag{3.25}$$

where

$$A_j(t)=\frac{(j\,|m(t))}{(j\,|j)}\,, \tag{3.26}$$

and, in particular, where

$$A_0(t)=\frac{(m(0)\,|m(t))}{(m(0)\,|m(0))}\equiv\frac{G(t)}{G(0)}\,. \tag{3.27}$$

That is, the projection of the rotating vector $|m(t))$ on the first orthogonal function $|0)$ is essentially the autocorrelation being sought. Note that initially the vector $|m(t))$ lies wholly in the $|0)$ direction, i.e.,

$$A_0(0)=1,\quad A_j(0)=0,\quad j>0\,. \tag{3.28}$$

The coefficients $A_j(t)$ are functions of the time alone and we can easily obtain an equation for their time development from (3.22). Differentiating this equation with respect to time and using (3.25) on both sides, we get

$$\dot{A}_j(t)=i\sum_k A_k(t)\,\frac{(j\,|L\,|k)}{(j\,|j)}\,, \tag{3.29}$$

having used the orthogonality of the basis vectors $|j)$. Now, from the definitions (3.24), it is apparent that $L$ will expand a vector $|k)$ onto the subset of vectors $\{|k+1),\ |k),\ \ldots,\ |0)\}$, and so we write

$$L\,|k)=|k+1)+\sum_{l=0}^{k}\Gamma_{lk}\,|l) \tag{3.30}$$

and, for the Hermitian conjugate,

$$(k\,|L=(k+1\,|+\sum_{l=0}^{k}\Gamma_{lk}^{\dagger}(l\,|\,, \tag{3.31}$$

where the matrix $\Gamma_{lk}$ is to be determined. But for

any vector $|j)$, $j \leq k$, it follows that [use (3.30) in the first line and (3.31) in the second]

$$(j|L|k) = \Gamma_{jk}(j|j) \tag{3.32}$$

$$= (j+1|j+1)\delta_{j+1,k} + \Gamma^{\dagger}_{jj}(j|j)\delta_{jk}\,, \tag{3.33}$$

so that

$$\Gamma_{jk} = \frac{(j+1|j+1)}{(j|j)}\,\delta_{j+1,k} + \Gamma^{\dagger}_{jj}\,\delta_{jk}\,. \tag{3.34}$$

Now define the parameters

$$\omega_j \equiv \Gamma_{jj} = \frac{(j|L|j)}{(j|j)}\,, \tag{3.35}$$

$$\nu_j^2 \equiv \Gamma_{j,j+1} = \frac{(j+1|j+1)}{(j|j)} \geq 0\,. \tag{3.36}$$

Then combining (3.30), (3.34), and the two equations above, we find that $L$ spreads $|k)$ out onto three successive vectors

$$L|k) = |k+1) + \omega_k|k) + \nu_{k-1}^2|k-1)\,, \tag{3.37}$$

and hence that

$$\frac{(j|L|k)}{(j|j)} = \delta_{j,k+1} + \omega_j\,\delta_{j,k} + \nu_j^2\,\delta_{j,k-1}\,. \tag{3.38}$$

Inserting this result in (3.29), we have the desired equations for the $A_j(t)$

$$\begin{aligned} -i\dot{A}_0(t) &= \omega_0 A_0(t) + \nu_0^2 A_1(t)\,, \\ -i\dot{A}_j(t) &= A_{j-1}(t) + \omega_j A_j(t) + \nu_j^2 A_{j+1}(t)\,, \quad j>0\,. \end{aligned} \tag{3.39}$$

These equations may be conveniently solved (at least formally) in Laplace-transform representation. We write the Laplace transform of a function $f(t)$ as

$$\hat{f}(z) = \int_0^{\infty} dt\, e^{-zt} f(t)\,. \tag{3.40}$$

Then, the transformed Eqs. (3.39) read

$$\begin{aligned} -i[z\hat{A}_0(z) - A_0(0)] &= \omega_0\hat{A}_0(z) + \nu_0^2\hat{A}_1(z)\,, \\ -i[z\hat{A}_j(z) - A_j(0)] &= \hat{A}_{j-1}(z) + \omega_j\hat{A}_j(z) + \nu_j^2\hat{A}_{j+1}(z), \\ & \qquad j>0\,. \end{aligned} \tag{3.41}$$

Now we can incorporate the initial values given in (3.28), obtaining finally an infinite set of simultaneous algebraic equations for the coefficients $\hat{A}_j(z)$:

$$\begin{aligned} (iz+\omega_0)\hat{A}_0(z) + \nu_0^2\hat{A}_1(z) &= i\,, \\ \hat{A}_{j-1}(z) + (iz+\omega_j)\hat{A}_j(z) + \nu_j^2 A_{j+1}(z) &= 0\,, \end{aligned} \tag{3.42}$$

or, in matrix notation,

$$\begin{pmatrix} iz+\omega_0 & \nu_0^2 & 0 & \cdots \\ 1 & iz+\omega_1 & \nu_1^2 & \cdots \\ 0 & 1 & iz+\omega_2 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} \hat{A}_0(z) \\ \hat{A}_1(z) \\ \hat{A}_2(z) \\ \vdots \end{pmatrix} = \begin{pmatrix} i \\ 0 \\ 0 \\ \vdots \end{pmatrix}. \tag{3.43}$$

As noted earlier, $A_0(t)$ is proportional to the autocorrelation function $G(t)$. Using Cramer's rule to obtain its Laplace transform from (3.43), we have, finally, the solution

$$\hat{G}(z)/G(0) \equiv \hat{A}_0(z) = i\mathfrak{D}_1(z)/\mathfrak{D}_0(z)\,, \tag{3.44}$$

where $\mathfrak{D}_j(z)$ is an infinite-order determinant of the form

$$\mathfrak{D}_j(z) = \begin{vmatrix} iz+\omega_j & \nu_j^2 & 0 & \cdots \\ 1 & iz+\omega_{j+1} & \nu_{j+1}^2 & \cdots \\ 0 & 1 & iz+\omega_{j+2} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{vmatrix}. \tag{3.45}$$

In principle, Eq. (3.44) is a complete solution to the problem originally posed, in that it provides an explicit expression for the Laplace transform of $G(t)$ from which, by Laplace inversion, the autocorrelation function at all times may be found. In practice, of course, one must contend with the fact that, as with the moments, only a few of the coefficients $\omega_j$ and $\nu_j^2$ will actually be known, so that at some point approximations are inevitable. The advantage of this formal solution, however, lies in the guidance it can give to the selection and systematic ordering of possible approximations, and the efficient use it can make of the actual information available. These comments will be clarified in the following sections.

Before continuing, it is necessary to give the ratio of infinite determinants appearing in (3.44) a more precise meaning. This may be done by returning to the original expansion of $|m(t))$, Eq. (3.25), and considering a finite version, whereby only the first $n+1$ orthogonal vectors are used to represent $|m(t))$, i.e.,

$$|m(t))^{(n)} = \sum_{j=0}^{n} A_j(t)\,|j)\,. \tag{3.46}$$

The previous solution will then be recovered in the limit as $n$ goes to infinity. Proceeding from (3.46) exactly as before, we now obtain a solution for $\hat{A}_0(z)$ as a ratio of finite determinants

$$\hat{A}_0^{(n)}(z) = i\,\mathfrak{D}_1^{(n)}(z)/\mathfrak{D}_0^{(n)}(z)\,, \tag{3.47}$$

where

$$\mathfrak{D}_j^{(n)}(z)=\begin{vmatrix} iz+\omega_j & \nu_j^2 & 0 & \cdots & 0 \\ 1 & iz+\omega_{j+1} & \nu_{j+1}^2 & \cdots & 0 \\ 0 & 1 & iz+\omega_{j+2} & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \cdots & iz+\omega_n \end{vmatrix} . \tag{3.48}$$

The infinite-order solution is then obtained by defining

$$\frac{\mathfrak{D}_1(z)}{\mathfrak{D}_0(z)} \equiv \lim_{n\to\infty} \frac{\mathfrak{D}_1^{(n)}(z)}{\mathfrak{D}_0^{(n)}(z)} . \tag{3.49}$$

Note that, for any finite $n$, $\mathfrak{D}_j^{(n)}(z)$ is a polynomial in $z$ of degree $n+1-j$, so that the denominator in (3.49) is a polynomial of one degree higher than the numerator, a fact which determines the asymptotic form of the ratio. That is, for large $z$, (3.44) becomes

$$A_0(z) \sim 1/z , \quad z\to\infty . \tag{3.50}$$

This is consistent with the obvious fact that

$$A_0(t) \underset{t\to 0}{\to} 1 . \tag{3.51}$$

### D. Memory Function and Continued Fractions

By expanding in minors of the first row, one easily obtains a recursion relation for the determinants $\mathfrak{D}_j(z)$:

$$\mathfrak{D}_j(z) = (iz+\omega_j)\mathfrak{D}_{j+1}(z) - \nu_j^2 \mathfrak{D}_{j+2}(z) . \tag{3.52}$$

Applied to the denominator in (3.44), this rule produces the form

$$\frac{\hat{G}(z)}{G(0)} = \frac{i\mathfrak{D}_1(z)}{(iz+\omega_0)\mathfrak{D}_1(z) - \nu_0^2\mathfrak{D}_2(z)} = \frac{1}{z - i\omega_0 + \nu_0^2 i\mathfrak{D}_2(z)/\mathfrak{D}_1(a)} = \frac{1}{z - i\omega_0 + \hat{K}(z)} , \tag{3.53}$$

where we have put

$$\hat{K}(z) = \nu_0^2\, i\mathfrak{D}_2(z)/\mathfrak{D}_1(z) . \tag{3.54}$$

The role of this function may be seen as follows. Rewrite (3.53) in the form

$$z\hat{G}(z) - G(0) = i\omega_0\hat{G}(z) - \hat{G}(z)\hat{K}(z) , \tag{3.55}$$

and perform a Laplace inversion to get

$$\frac{dG(t)}{dt} = i\omega_0 G(t) - \int_0^t dt'\, K(t-t')G(t') . \tag{3.56}$$

That is, $K(t)$ is a memory function of the dynamical system, giving the weight to be assigned to previous values of $G(t)$ in computing its present rate of change. Clearly, a knowledge of $K(t)$ completely determines the autocorrelation function $G(t)$. The memory function defined in (3.54) is, of course, no easier to determine than $\hat{G}(z)$ itself. However, as will be shown later, it is less sensitive to approximations, so that Eqs. (3.54) and (3.56) are a convenient point of departure for approximate solutions of $G(t)$.

Alternatively, one may relate $G(t)$ and $K(t)$ through their Fourier transforms. We note first that since

$$\tilde{G}(\omega) = (1/2\pi)\int_{-\infty}^{\infty} dt\, e^{-i\omega t}G(t) , \tag{3.57}$$

we may write

$$\begin{aligned}\tilde{G}(\omega) &= (1/2\pi)\int_0^\infty dt[e^{-i\omega t}G(t) + e^{i\omega t}G(-t)] \\ &= (1/2\pi)\int_0^\infty dt\{[e^{-i\omega t}G(t)] + [e^{-i\omega t}G(t)]^*\} \\ &= (1/2\pi)[\hat{G}(i\omega) + \hat{G}^*(i\omega)] = (1/\pi)\,\mathrm{Re}\hat{G}(i\omega) ,\end{aligned} \tag{3.58}$$

where we used Eqs. (2.63). Since the Laplace transform $\hat{G}(z)$ is defined only for points $z$ in the right half plane, i.e., $\mathrm{Re}(z) > 0$, $\hat{G}(i\omega)$ should be understood in the sense of a limit from the right-hand side:

$$\hat{G}(i\omega) = \lim_{\epsilon\to 0^+} \hat{G}(\epsilon + i\omega) . \tag{3.59}$$

Then, from (3.53), we have

$$\hat{G}(i\omega) = [i(\omega-\omega_0) + \hat{K}(i\omega)]^{-1} , \tag{3.60}$$

where

$$\hat{K}(i\omega) = \int_0^\infty dt\, e^{-i\omega t}K(t) = K'(\omega) - iK''(\omega) , \tag{3.61}$$

with the real and imaginary parts given by

$$K'(\omega) = \int_0^\infty dt K(t)\cos\omega t , \tag{3.62}$$

$$K''(\omega) = \int_0^\infty dt K(t)\sin\omega t . \tag{3.63}$$

Using (3.61) in (3.60) and taking the real part of the result, we get, finally,

$$\tilde{G}(\omega) = \frac{1}{\pi}\,\frac{G(0)K'(\omega)}{[\omega-\omega_0-K''(\omega)]^2 + [K'(\omega)]^2} , \tag{3.64}$$

from which it is seen that the imaginary part $K''(\omega)$ leads to a shift in the spectral line originally centered at $\omega_0$, and the real part $K'(\omega)$ accounts for a broadening of the line. In this form, a knowledge of the memory function leads directly to a solution of the line-shape problem of $\tilde{G}(\omega)$ and hence to that of the relaxation function $\tilde{F}(\omega)$ through Eqs. (2.54) and (2.62). In Sec. IV, we shall con-

sider several approximations for the memory function $K(t)$.

Repeated use of the recursion relation (3.52) leads to an expression for $\hat{G}(z)$ that lends itself to systematic approximation. Beginning with

$$\hat{G}(z) = G(0) i \mathfrak{D}_1(z)/\mathfrak{D}_0(z) , \tag{3.65}$$

we saw that use of (3.52) produced the form

$$\hat{G}(z) = \frac{G(0)}{z - i\omega_0 + \nu_0^2 i \mathfrak{D}_2(z)/\mathfrak{D}_1(z)} . \tag{3.66}$$

If $\mathfrak{D}_1(z)$ is again expanded using (3.52), we get

$$\hat{G}(z) = \frac{G(0)}{z - i\omega_0 + \dfrac{\nu_0^2}{z - i\omega_1 + \nu_1^2 i \mathfrak{D}_3(z)/\mathfrak{D}_2(z)}} . \tag{3.67}$$

Continuing in this fashion, repeated use of (3.52) on the determinant in the denominator produces an infinite continued fraction for $\hat{G}(z)$,

$$\hat{G}(z) = \cfrac{G(0)}{z - i\omega_0 + \cfrac{\nu_0^2}{z - i\omega_1 + \cfrac{\nu_1^2}{z - i\omega_2 + \ddots}}} , \tag{3.68}$$

which was first obtained by Mori.[8] A similar representation can be given for the memory-function transform $\hat{K}(z)$ and indeed for any ratio $i \mathfrak{D}_{j+1}(z)/\mathfrak{D}_j(z)$.

### E. Orthogonal Polynomials

What has been done in the previous sections amounts, in practical terms, to a recasting of the original problem in a new form that may be more suitable for motivating approximations, rather than a computable solution in itself. In particular, the new form is one that is well known in mathematical analysis as the classical-moment problem and is intimately connected with the general theory of orthogonal polynomials.[26] Indeed, the finite determinants $\mathfrak{D}_0^{(j)}(z)$ constitute, as will be shown below, the orthogonal polynomials characteristic of the problem. In this section, we will consider several general properties of these polynomials.

The determinants $\mathfrak{D}_0^{(j)}(z)$, defined in (3.48), satisfy a recursion relation similar to (3.52) which may be obtained by expanding in minors of the $j$th row or column

$$\mathfrak{D}_0^{(j)}(z) = (iz + \omega_j)\mathfrak{D}_0^{(j-1)}(z) - \nu_{j-1}^2 \mathfrak{D}_0^{(j-2)}(z) . \tag{3.69}$$

The lowest-order polynomial defined by (3.48) is

$$\mathfrak{D}_0^{(0)}(z) = iz + \omega_0 , \tag{3.70}$$

and for convenience of notation we adopt the convention that

$$\mathfrak{D}_0^{(-1)}(z) = 1. \tag{3.71}$$

We now note that (3.69) is formally similar to the recursion relation of the orthogonal functions, Eq. (3.37), which can be written

$$|j+1) = (L - \omega_j)|j) - \nu_{j-1}^2 |j-1). \tag{3.72}$$

When supplemented with the first two vectors from (3.24),

$$\begin{aligned} |0) &= |m(0)) , \\ |1) &= (L - \omega_0)|m(0)) , \end{aligned} \tag{3.73}$$

Eq. (3.72) can be used to generate the remaining vectors. But the vectors $|0)$ and $|1)$ evidently can be written

$$\begin{aligned} |0) &= \mathfrak{D}_0^{(-1)}(iL)|m(0)) , \\ |1) &= -\mathfrak{D}_0^{(0)}(iL)|m(0)) , \end{aligned} \tag{3.74}$$

and if we put, in general,

$$|j) = (-1)^j \mathfrak{D}_0^{(j-1)}(iL)|m(0)) , \tag{3.75}$$

then the recursion relation (3.69) for the determinants reproduces (3.72) for the vectors. It follows, therefore, by mathematical induction that all the orthogonal vectors can be written in the form (3.75), where $\mathfrak{D}_0^{(j)}(iL)$ is a Hermitian polynomial operator. As will now be shown, the polynomials $\mathfrak{D}_0^{(j)}(z)$ are themselves orthogonal. We note in passing that, in this view, the expansion (3.25) is an expansion of the exponential operator in orthogonal polynomial operators,

$$e^{itL} = \sum_{j=0}^{\infty} (-1)^j A_j(t) \mathfrak{D}_0^{(j-1)}(iL) . \tag{3.76}$$

The orthogonality of the $\mathfrak{D}_0^{(j)}(z)$ may be proved in the following way. We have constructed the basis set $|j)$ so that

$$(l|j) = (j|j)\delta_{lj} . \tag{3.77}$$

Now using (3.75) and the Hermitian nature of $L$, the left-hand side of (3.77) may be written

$$\begin{aligned} (l|j) &= (-1)^{l+j} (m(0)|\mathfrak{D}_0^{(l-1)}(iL)\mathfrak{D}_0^{(j-1)}(iL)|m(0)) \\ &= (-1)^{l+j} (m(0)|\,(1/2\pi i)\int_C dz\, \mathfrak{D}_0^{(l-1)}(z)\mathfrak{D}_0^{(j-1)}(z) \\ &\qquad \times (z - iL)^{-1}|m(0)) \\ &= \frac{(-1)^{l+j}}{2\pi i}\int_C dz\, \mathfrak{D}_0^{(l-1)}(z)\mathfrak{D}_0^{(j-1)}(z) \\ &\qquad \times (m(0)|\,(z - iL)^{-1}|m(0)) \end{aligned}$$

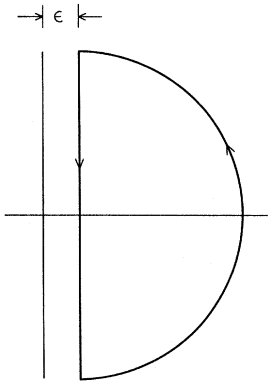


FIG. 2. Contour for the integral in Eq. (3.78).

$$= \frac{(-1)^{i+j}}{2\pi i} V \int_C dz\, \hat{G}(z)\, \mathfrak{D}_0^{(i-1)}(z)\, \mathfrak{D}_0^{(j-1)}(z) . \quad (3.78)$$

In obtaining this result, we made formal use of Cauchy's integral formula and recognized that

$$\hat{G}(z) \equiv \int_0^\infty dt\, e^{-zt} G(t) = (1/V) \int_0^\infty dt\, e^{-zt} (m(0) | e^{itL} | m(0))$$

$$= (1/V)(m(0) | (z - iL)^{-1} | m(0)) . \quad (3.79)$$

The contour $C$ of the complex integration is shown in Fig. 2. When (3.78) is equated to the right-hand side of (3.77), we get the desired result:

$$\frac{1}{2\pi i} \int_C dz\, \hat{G}(z)\, \mathfrak{D}_0^{(i)}(z)\, \mathfrak{D}_0^{(j)}(z) = \frac{(j+1 | j+1)}{V} \delta_{ij}$$

$$= \frac{(j+1 | j+1)}{(j | j)} \frac{(j | j)}{(j-1 | j-1)} \cdots \frac{(0 | 0)}{V} \delta_{ij}$$

$$= \left( \prod_{s=0}^{j} \nu_s^2 \right) G(0) \delta_{ij} . \quad (3.80)$$

That is, the determinants $\mathfrak{D}_0^{(j)}(z)$ constitute orthogonal polynomials in the complex plane with weight function $\hat{G}(z)/G(0)$. The polynomials could be normalized by dividing each $\mathfrak{D}_0^{(j)}(z)$ by $\prod_{s=0}^{j} \nu_s$ .

The orthogonality integral may also be written in real terms. To do this, we need a relation between the Laplace and Fourier transforms of $G(t)$ which is proved in the Appendix, namely,

$$\hat{G}(z) = \int_{-\infty}^{\infty} d\omega \frac{\tilde{G}(\omega)}{z - i\omega - \epsilon} , \quad \mathrm{Re}(z) > \epsilon . \quad (3.81)$$

Then inserting this result into (3.80), we get

$$\int_{-\infty}^{\infty} d\omega \tilde{G}(\omega) \frac{1}{2\pi i} \int_C dz \frac{\mathfrak{D}_0^{(i)}(z)\, \mathfrak{D}_0^{(j)}(z)}{z - i\omega - \epsilon}$$

$$= \int_{-\infty}^{\infty} d\omega\, \tilde{G}(\omega)\, \mathfrak{D}_0^{(i)}(i\omega)\, \mathfrak{D}_0^{(j)}(i\omega) \quad (3.82)$$

in the left-hand side, having again used Cauchy's integral formula and having taken the limit of vanishing $\epsilon$. The orthogonality relation (3.80) thus becomes

$$\int_{-\infty}^{\infty} d\omega\, \tilde{G}(\omega)\, \mathfrak{D}_0^{(i)}(i\omega)\, \mathfrak{D}_0^{(j)}(i\omega) = \left( \prod_{s=0}^{j} \nu_s^2 \right) G(0) \delta_{ij} , \quad (3.83)$$

so that the real polynomials $\mathfrak{D}_0^{(j)}(i\omega)$ are seen to be orthogonal with respect to the weight function $\tilde{G}(\omega)/G(0)$.

### F. Coefficients $\omega_j$ and $\nu_j^2$ ; Approximants

Given the close connection between the moment expansion and the orthogonal expansion, it is to be expected that the coefficients $\omega_j$ and $\nu_j^2$ of the latter are closely related to the moments $M_j$ of the former. The explicit relation is presented in this section.

Define the Hankel determinant

$$D_j = \begin{vmatrix} 1 & M_1 & \cdots & M_j \\ M_1 & M_2 & \cdots & M_{j+1} \\ \vdots & \vdots & \ddots & \vdots \\ M_j & M_{j+1} & \cdots & M_{2j} \end{vmatrix} , \quad (3.84)$$

where the $M_k$ are the moments defined in (3.17) and (3.21). It is shown by Akhiezer[26] that, in terms of these determinants,

$$\nu_j^2 = D_{j-1} D_{j+1} / D_j^2 , \quad (3.85)$$

from which it is evident that $\nu_j^2$ depends on the first $2j+2$ moments.

The $\omega_j$ are given by (3.35). This expression can be somewhat simplified as follows. From the generating equation (3.24), we have

$$L | j) = L^{j+1} | 0) - \sum_{k=0}^{j-1} \frac{(k | L^j | 0)}{(k | k)} L | k)$$

$$= | j+1) + \sum_{k=0}^{j} \frac{(k | L^{j+1} | 0)}{(k | k)} | k) - \sum_{k=0}^{j-1} \frac{(k | L^j | 0)}{(k | k)} L | k) . \quad (3.86)$$

By iterating this equation for $L | k)$ once, we bring out all the dependence of $L | j)$ on $| j)$, which leads to

$$\omega_j = \frac{(j | L | j)}{(j | j)} = \frac{(j | L^{j+1} | 0)}{(j | j)} - \frac{(j-1 | L^j | 0)}{(j-1 | j-1)} , \quad (3.87)$$

or, by successive applications of this result,

$$\omega_j = \frac{(j | L^{j+1} | 0)}{(j | j)} - \sum_{k=0}^{j-1} \omega_k . \quad (3.88)$$

Thus, $\omega_j$ depends on the first $2j+1$ moments.

Explicitly, the first few coefficients are

$$\omega_0 = M_1 \ , \quad \nu_0^2 = M_2 - M_1^2 \ ,$$
$$\omega_1 = \frac{M_3 - M_1 M_2}{\nu_0^2} - \omega_0 \ , \tag{3.89}$$
$$\nu_1^2 = \frac{M_4 - M_2^2}{\nu_0^2} - (\omega_0 + \omega_1)^2 \ .$$

In connection with these relations, we note that $\mathfrak{D}_0^{(j)}(z)$ contains the moments $M_k$ up to and including $M_{2j+1}$. By expanding in inverse powers of $z$, it can be shown[28] that

$$i\frac{\mathfrak{D}_1^{(j)}(z)}{\mathfrak{D}_0^{(j)}(z)} = \frac{1}{z} + \frac{M_1}{z^2} + \cdots + \frac{M_{2j+1}}{z^{2j+2}} + O\left(\frac{1}{z^{2j+3}}\right) \ . \tag{3.90}$$

That is, this ratio is an *approximant* of $\hat{G}(z)$, giving correctly the first $2j+2$ terms of the moment expansion of $G(t)$.

The first moment $M_1 = \omega_0$ gives the center of the distribution $\tilde{G}(\omega)$. In many cases, this distribution is symmetric about $\omega_0$, so that the central moments

$$M_j' = \langle (\omega - \omega_0)^j \rangle = \frac{(0|(L-\omega_0)^j|0)}{(0|0)} \tag{3.91}$$

vanish for $j$ odd. For such cases, all the $\omega_j$ are identical:

$$\omega_j = \omega_0 \ \text{ for all } j \ . \tag{3.92}$$

This is evidently so for $\omega_1$, which from (3.89), may be written

$$\omega_1 = \omega_0 + M_3'/M_2' = \omega_0 \ , \tag{3.93}$$

since $M_3' = 0$. Assume (3.92) is correct for $\omega_1, \ldots, \omega_{j-1}$. Then, using (3.35) and (3.75), we have

$$\omega_j = \frac{(0|L[\mathfrak{D}_0^{(j-1)}(iL)]^2|0)}{(0|[\mathfrak{D}_0^{(j-1)}(iL)]^2|0)}$$
$$= \omega_0 + \frac{(0|(L-\omega_0)[\mathfrak{D}_0^{(j-1)}(iL)]^2|0)}{(0|[\mathfrak{D}_0^{(j-1)}(iL)]^2|0)} \ . \tag{3.94}$$

But $\mathfrak{D}_0^{(j-1)}(iL)$ is a polynomial in $(L-\omega_0)$, so that the operator in the numerator in (3.94) will appear as a sum of *odd* powers of $(L-\omega_0)$, leading to a sum of odd central moments which vanish. Hence, if (3.92) is valid for $\omega_1$, it is thus valid for all $\omega_j$.

It is convenient for these cases to introduce the simpler correlation and memory functions $G_1(t)$ and $K_1(t)$, defined by

$$G(t) = e^{i\omega_0 t} G_1(t) \ , \quad K(t) = e^{i\omega_0 t} K_1(t) \ , \tag{3.95}$$

so that, from Eq. (3.56),

$$\frac{dG_1(t)}{dt} = -\int_0^t dt' K_1(t-t') G_1(t') \ . \tag{3.96}$$

In terms of the Laplace transforms, these relations are

$$\hat{G}(z + i\omega_0) = \hat{G}_1(z) \ , \quad \hat{K}(z + i\omega_0) = \hat{K}_1(z) \ , \tag{3.97}$$

and

$$\hat{G}_1(z) = G_1(0)/[z + \hat{K}_1(z)] \ . \tag{3.98}$$

The results obtained in previous sections for $G(t)$ and $K(t)$ can be applied to $G_1(t)$ and $K_1(t)$ merely by setting all $\omega_j$ to zero and interpreting the moments in (3.84) for $\nu_j^2$ as central moments.

## IV. APPROXIMATE EVALUATION OF TIME-AUTOCORRELATION FUNCTION

### A. Approximate Memory Functions

In Sec. III we have presented a formal solution to the problem of calculating time-autocorrelation functions. Like the moment expansion from which it is descended, this solution requires a knowledge of all the moments of the corresponding spectral function, clearly a hopeless demand. In contrast to the moment expansion, however, the present formulation is able to make efficient use of those few moments that will in practice be available. In addition, the formalism may suggest specific functional forms for desired correlations, containing perhaps a small number of parameters which, though not obtainable from within the formalism, may be readily gotten from experiment.

In Sec. IV B, we will consider one possible resolution of the practical difficulties arising from the limited data available, based on a perturbationlike calculation. In the present section, the problem will first be approached by constructing approximate models of the memory function $K(t)$. In both sections, we shall assume for simplicity that $\tilde{G}(\omega)$ is symmetric about $\omega = \omega_0$, enabling us to use the simpler functions $G_1(t)$ and $K_1(t)$ of Eqs. (3.95) if desired.

Equation (3.96), relating the correlation and memory functions, provides a solution for the former once the latter is known. Clearly, what is wanted here is a second, albeit approximate, equation expressing $K_1(t)$ as a functional of $G_1(t)$, so that (3.96) becomes a nonlinear integral equation for the single unknown $G_1(t)$, whose iterative solution then generates an infinite sum of contributions which approximates the moment expansion to all orders. With the exception of the system of equations obtained by the Prigogine school,[23] which are limited by severe mathematical difficulties, such a procedure is not yet available, and in the following we consider only various explicit forms for $K_1(t)$ not depending on $G_1(t)$.

The simplest of these corresponds to the solution of the Bloch equations and may be motivated as follows. The area under the normalized correlation function $G_1(t)/G_1(0)$ is given by its Laplace trans-

form $\hat{G}_1(0)/G_1(0)$ evaluated at $z=0$. From (3.98), it is seen that this area is inversely proportional to that under $K_1(t)$, suggesting that if $G_1(t)$ is relatively long ranged, then $K_1(t)$ will be comparatively short ranged. Proceeding on this assumption, we note that $K_1(t-t')$ in (3.96) will be significant only for times $t'$ near $t$, so that we might approximate the integral by writing (Markoffian approximation)

$$\frac{dG_1(t)}{dt} \approx -G_1(t)\int_0^t dt' K_1(t-t') \approx -G_1(t)\hat{K}_1(0) \tag{4.1}$$

for sufficiently long times $t$. In this approximation, therefore, $G_1(t)$ is an exponential function

$$G_1(t) = G_1(0)e^{-t/T}, \quad t>0 \tag{4.2}$$

with a decay time $T=[\hat{K}_1(0)]^{-1}$, and correspondingly the line shape $\tilde{G}(\omega)$ is Lorentzian

$$\tilde{G}(\omega) = \tilde{G}_1(\omega-\omega_0) = \frac{TG(0)}{\pi}\,\frac{1}{1+(\omega-\omega_0)^2T^2}\,. \tag{4.3}$$

Since it depends on all the moments, the decay time $T$ is not computable here and must be obtained from experiment.

It is evident that (4.1) corresponds to approximating

$$\hat{K}_1(z) \equiv i\nu_0^2 \mathfrak{D}_2(z)/\mathfrak{D}_1(z) \tag{4.4}$$

in Eq. (3.98) by its limiting value at $z=0$. [The determinants $\mathfrak{D}_j(z)$ here are to be understood according to the comments in the last paragraph of Sec. III F.] This is the first of the sequence of "long-time approximations" of Mori,[8] obtained in general by neglecting the $z$ dependence of the ratio $i\nu_j^2\mathfrak{D}_{j+2}(z)/\mathfrak{D}_{j+1}(z)$. Thus, in the next approximation with $j=1$, we write for the Laplace transform of the memory function [Eq. (3.67)]

$$\hat{K}_1(z) = \nu_0^2/(z+\lambda_1)\,, \tag{4.5}$$

where, in general,

$$\lambda_j = i\nu_j^2\mathfrak{D}_{j+2}(0)/\mathfrak{D}_{j+1}(0) \tag{4.6}$$

or, in this case,

$$\lambda_1 = \nu_0^2[\hat{K}_1(0)]^{-1} = \nu_0^2 T\,. \tag{4.7}$$

This leads to an exponential memory function

$$K_1(t) = \nu_0^2 e^{-\lambda_1 t}\,, \quad t>0 \tag{4.8}$$

and, depending on the numerical values of $\nu_0$ and $T$, the correlation function may in this case display an oscillatory behavior. We have, from (4.5),

$$\hat{G}_1(z) = G_1(0)\,\frac{z+\lambda_1}{z^2+\lambda_1 z+\nu_0^2} = \frac{G_1(0)}{z_+-z_-}\left(\frac{z_++\lambda_1}{z-z_+} - \frac{z_-+\lambda_1}{z-z_-}\right), \tag{4.9}$$

with

$$z_\pm = -\tfrac{1}{2}\lambda_1 \pm \tfrac{1}{2}(\lambda_1^2-4\nu_0^2)^{1/2}\,, \tag{4.10}$$

so that, by Laplace inversion,

$$G_1(t) = [G_1(0)/z_+-z_-][(z_++\lambda_1)e^{z_+t} - (z_-+\lambda_1)e^{z_-t}]\,, \quad t>0\,. \tag{4.11}$$

If $\nu_0$ and $T$ are such that

$$\lambda_1^2 - 4\nu_0^2 = -4\alpha^2 < 0\,, \tag{4.12}$$

then (4.11) becomes

$$G_1(t) = G_1(0)e^{-(1/2)\lambda_1 t}[\cos\alpha t + (\lambda_1/2\alpha)\sin\alpha t]\,, \quad t>0 \tag{4.13}$$

a damped oscillatory function.

Higher approximations can be found in the same way. In order to apply the approximation (4.6) for a given $j$, it is necessary to know $\nu_0^2$, $\nu_1^2$, ..., $\nu_{j-1}^2$ and the decay time $T$.

Equations such as (4.2) and (4.11) cannot be correct, in general, since their expansions contain odd powers of $t$, whereas the odd central moments of $G(t)$ all vanish, by assumption. A convenient one-parameter model of the memory function which correctly incorporates this property is the Gaussian memory

$$K_1(t) = \nu_0^2 e^{-Bt^2}\,, \tag{4.14}$$

studied by several authors.[22-24] The constant $B$ is usually chosen so that the resulting correlation function $G_1(t)$ yields the correct fourth central moment $M_4'$. Borckmans and Walgraef[22,23] have shown that in the long-time limit, Eq. (4.14) leads to a damped oscillatory correlation function of the form of (4.13).

Finally, using the method of retarded Green's functions, Mansfield[25] has shown that satisfactory agreement with experiment for solid $CaF_2$ can be obtained by taking, in effect,

$$K_1(t) = \nu_0^2\,\theta(\tau-t)\,, \tag{4.15}$$

where $\theta(x)$ is the unit step function

$$\theta(x) = \begin{cases} 1, & x>0 \\ 0, & x<0 \end{cases} \tag{4.16}$$

and $\tau$ is a correlation time determined from the first two even moments of $\tilde{G}_1(\omega)$.

The generally good agreement with experiment which is obtained using the exponential, Gaussian, or step-function memories discussed above suggests that, at least in the case of the fluorine resonance in solid $CaF_2$, the correlation function $G_1(t)$ is not very sensitive to the detailed shape of the memory function $K_1(t)$.

### B. Perturbation Expansion for $G_1(z)$

Usually, one knows about the spectral function $\tilde{G}_1(\omega)$ to be calculated its approximate shape in

terms of simple functions and its first few moments. In this section, we consider one way, essentially a perturbation-type expansion, in which this limited information might be used to construct an approximate solution.

Suppose, for example, that $\tilde{G}_1(\omega)$ is known to be approximately Gaussian. The coefficients $\nu_j^2$ from Eqs. (3.84) and (3.85) (with the $M_j$ interpreted as central moments, so that $M_j = 0$ for odd $j$) may be written

$$\nu_0^2 = M_2' ,$$

$$\nu_1^2 = 2M_2' + \left[\frac{M_4' - 3M_2'^2}{M_2'}\right] , \tag{4.17}$$

$$\nu_2^2 = 3M_2' + \left[\frac{M_2'M_6' - M_4'^2 - 3M_2'^2M_4' + 3M_2'^4}{M_2'(M_4' - M_2'^2)}\right] , \text{ etc.}$$

If $\tilde{G}_1(\omega)$ were precisely Gaussian, each of the bracketed expressions in (4.17) would vanish. More generally, however, if $\tilde{G}_1(\omega)$ is approximately Gaussian, these terms are expected to represent small corrections to the initial (Gaussian) term of $\nu_j^2$. This suggests writing, for the general case,

$$\nu_j^2 = \nu_j^{\circ 2} + \delta_j , \tag{4.18}$$

where $\nu_j^{\circ 2}$ are the coefficients corresponding to the "unperturbed" case (e.g., the Gaussian) and the $\delta_j$ are (presumed small) correction terms, and where we are seeking a suitable expansion in powers of $\delta_j$.

Such an expansion may be obtained for the Laplace transform

$$\frac{\hat{G}_1(z)}{G_1(0)} = \lim_{n\to\infty} i\frac{\mathfrak{D}_1^{(n)}(z)}{\mathfrak{D}_0^{(n)}(z)} \tag{4.19}$$

by means of a generalized recursion relation of the polynomials $\mathfrak{D}_j^{(n)}(z)$. In addition to the relations (3.52) and (3.69) already given, Muir and Metzler[29] show that these polynomials satisfy more generally

$$\mathfrak{D}_j^{(n)}(z) = \mathfrak{D}_j^{(k)}(z)\mathfrak{D}_{k+1}^{(n)}(z) - \nu_k^2\mathfrak{D}_j^{(k-1)}(z)\mathfrak{D}_{k+2}^{(n)}(z) \tag{4.20}$$

for $j \leqq k < n$, where the convention

$$\mathfrak{D}_{k+1}^{(k)}(z) = 1 \tag{4.21}$$

has been adopted for the sake of a more uniform presentation. Equation (4.20) includes (3.52) and (3.69) as special cases.

We will need temporarily a hybrid determinant $\mathfrak{D}_{j;s}^{(n)}(z)$ which is defined to contain the unperturbed $\nu_i^{\circ 2}$ for $j \leqq i \leqq s$ and the complete $\nu_i^2$ for $s < i < n$. Then, choosing $k = j$ in (4.20), we write

$$\mathfrak{D}_j^{(n)}(z) = \mathfrak{D}_j^{(j)}(z)\,\mathfrak{D}_{j+1}^{(n)}(z) - (\nu_j^{\circ 2} + \delta_j)\,\mathfrak{D}_j^{(j-1)}(z)\,\mathfrak{D}_{j+2}^{(n)}(z)$$

$$= \mathfrak{D}_{j;j}^{(n)}(z) - \delta_j\mathfrak{D}_j^{\circ\,(j-1)}(z)\mathfrak{D}_{j+2}^{(n)}(z) , \tag{4.22}$$

where a superscript degree mark on $\mathfrak{D}$ will identify a determinant containing only unperturbed $\nu_j^\circ$. Continuing, the same operations are now performed on the hybrid determinant of (4.22) with the choice $k = j+1$, which gives

$$\mathfrak{D}_j^{(n)}(z) = \mathfrak{D}_{j;j}^{(j+1)}(z)\mathfrak{D}_{j+2;j}^{(n)}(z) - (\nu_{j+1}^{\circ 2} + \delta_{j+1})\mathfrak{D}_{j;j}^{(j)}(z)\mathfrak{D}_{j+3;j}^{(n)}$$

$$- \delta_j\mathfrak{D}_j^{\circ\,(j-1)}(z)\mathfrak{D}_{j+2}^{(n)}(z)$$

$$= \mathfrak{D}_{j;j+1}^{(n)}(z) - \sum_{i=j}^{j+1}\mathfrak{D}_j^{\circ(i-1)}(z)\mathfrak{D}_{i+2}^{(n)}(z)\delta_i . \tag{4.23}$$

Continuing in this way successively through $k = n-1$, we obtain a discrete analog of an integral equation for $\mathfrak{D}_j^{(n)}(z)$

$$\mathfrak{D}_j^{(n)}(z) = \mathfrak{D}_j^{\circ\,(n)}(z) - \sum_{i=j}^{n-1}\mathfrak{D}_j^{\circ(i-1)}(z)\mathfrak{D}_{i+2}^{(n)}(z)\delta_i . \tag{4.24}$$

This equation may then be solved iteratively, giving the desired expansion of $\mathfrak{D}_j^{(n)}(z)$ in powers of the corrections $\delta_i$:

$$\mathfrak{D}_j^{(n)}(z) = \mathfrak{D}_j^{\circ\,(n)}(z) - \sum_{i=j}^{n-1}\mathfrak{D}_j^{\circ(i-1)}\mathfrak{D}_{i+2}^{\circ(n)}(z)\delta_i$$

$$+ \sum_{i=j}^{n-1}\sum_{k=i+2}^{n-1}\mathfrak{D}_j^{\circ(i-1)}(z)\mathfrak{D}_{i+2}^{\circ(k-1)}(z)\mathfrak{D}_{k+2}^{\circ(n)}\delta_i\delta_k - \cdots . \tag{4.25}$$

This yields a representation of $\hat{G}_1(z)$

$$\frac{\hat{G}_1(z)}{G_1(0)} = i\mathfrak{D}_1^\circ(z) - \sum_{i=1}^{\infty}\mathfrak{D}_1^{\circ(i-1)}(z)\mathfrak{D}_{i+2}^\circ(z)\delta_i + \cdots$$

$$\times\,\mathfrak{D}_0^\circ(z) - \sum_{i=0}^{\infty}\mathfrak{D}_0^{\circ(i-1)}(z)\mathfrak{D}_{i+2}^\circ(z)\delta_i + \cdots \tag{4.26}$$

(having passed to the limit of infinite $n$) suitable for approximations. These can be made systematically by simply neglecting all corrections $\delta_j$ for $j$ greater than a given integer.

Thus, including only the first correction $\delta_0$, we get

$$\frac{\hat{G}_1(z)}{G_1(0)} \approx i\frac{\mathfrak{D}_1^\circ(z)}{\mathfrak{D}_0^\circ(z) - \mathfrak{D}_2^\circ(z)\delta_0}$$

$$= i\frac{\mathfrak{D}_1^\circ(z)}{\mathfrak{D}_0^\circ(z) - (\delta_0/\nu_0^{\circ 2})[iz\mathfrak{D}_1^\circ(z) - \mathfrak{D}_0^\circ(z)]}$$

$$= \frac{\nu_0^{\circ 2}\hat{G}_1^\circ(z)}{\nu_0^2 G_1^\circ(0) - z\hat{G}_1^\circ(z)\delta_0} , \tag{4.27}$$

where we have used (3.52) to eliminate $\mathfrak{D}_2^\circ(z)$. It is easily verified that (4.27) yields the correct asymptotic form (3.50), that is, $G_1(t)$ obtained from this equation is exact for short times. The approximation appears in the predicted long-time behavior. The asymptotic form of this long time $G_1(t)$ can be

obtained from (4.27) by locating (numerically if necessary) the root of the denominator with smallest real part.

Equation (4.27) can alternatively be written, by Laplace inversion, in the form of an integral equation for $G_1(t)$:

$$\frac{G_1(t)}{G_1(0)} \approx \frac{G_1^\circ(t)}{G_1^\circ(0)} + \frac{\delta_0}{\nu_0^{\circ 2}} \int_0^t dt' \frac{\dot{G}_1^\circ(t')}{G_1^\circ(0)} \frac{G_1(t-t')}{G_1(0)} , \tag{4.28}$$

where the dot denotes a time derivative.

Similarly, the next approximation, where only $\delta_0$ and $\delta_1$ are retained in (4.26), yields, after some simplification,

$$\frac{\hat{G}_1(z)}{G_1(0)} \approx \frac{(\nu_0^{\circ 2}\nu_1^2 + z^2\delta_1)\hat{G}_1^\circ(z) - z\delta_1 G_1^\circ(0)}{(\nu_0^2\nu_1^{\circ 2} - z^2\delta_1)G_1^\circ(0) + (\nu_0^{\circ 2}\delta_1 - \nu_1^{\circ 2}\delta_0 + z^2\delta_1)z\hat{G}_1^\circ(z)} \tag{4.29}$$

or, after Laplace inversion,

$$\frac{G_1(t)}{G_1(0)} \approx \frac{\nu_1^2}{\nu_1^{\circ 2}} \frac{G_1^\circ(t)}{G_1^\circ(0)} + \frac{\delta_1}{\nu_0^{\circ 2}\nu_1^{\circ 2}} \frac{\ddot{G}_1^\circ(t)}{G_1^\circ(0)} - \int_0^t dt' \left( \frac{\nu_0^{\circ 2}\nu_1^2 - \nu_0^2\nu_1^{\circ 2}}{\nu_0^{\circ 2}\nu_1^{\circ 2}} \frac{\dot{G}_1^\circ(t')}{G_1^\circ(0)} + \frac{\delta_1}{\nu_0^{\circ 2}\nu_1^{\circ 2}} \frac{\dddot{G}_1^\circ(t')}{G_1^\circ(0)} \right) \times \frac{G_1(t-t')}{G_1(0)} . \tag{4.30}$$

These equations reduce to the previous (4.27) and (4.28) upon setting $\delta_1$ to zero.

If higher coefficients are known, additional correction terms can be incorporated in the same manner. These equations are amenable to numerical solution.

## APPENDIX

In Eq. (3.58) it was readily shown that the Fourier transform of $G(t)$ could be obtained from the corresponding Laplace transform. Here we wish to demonstrate the inverse, that the Laplace transform of $G(t)$ can be expressed in terms of its Fourier transform. This relation was used in obtaining the orthogonality condition (3.83).

Let $z$ be a point contained within the contour C of Fig. 2. Then, since $\hat{G}(z)$ is analytic in the right plane, Cauchy's integral formula gives

$$\hat{G}(z) = \frac{1}{2\pi i} \int_C dz' \frac{\hat{G}(z')}{z' - z} = \frac{1}{2\pi i} \int_{-\infty}^{\infty} d\omega \frac{\hat{G}(\epsilon + i\omega)}{z - (\epsilon + i\omega)} , \tag{A1}$$

where we have used the fact that $\hat{G}(z)$ vanishes along the semicircular path as the radius becomes indefinitely large. Now, the real and imaginary parts of $\hat{G}(\epsilon + i\omega)$ satisfy the Kramers-Kronig relations, so that, in particular,

$$\mathrm{Im}\hat{G}(\epsilon + i\omega) = \frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} d\omega' \frac{\mathrm{Re}\hat{G}(\epsilon + i\omega')}{\omega' - \omega} , \tag{A2}$$

where $\mathcal{P}$ denotes the Cauchy principal value, and hence,

$$\int_{-\infty}^{\infty} d\omega \frac{\mathrm{Im}\hat{G}(\epsilon + i\omega)}{z - (\epsilon + i\omega)} = \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega' \, \mathrm{Re}\hat{G}(\epsilon + i\omega') \times \mathcal{P} \int_{-\infty}^{\infty} d\omega \frac{1}{[z - (\epsilon + i\omega)(\omega' - \omega)} = -i \int_{-\infty}^{\infty} d\omega' \frac{\mathrm{Re}\hat{G}(\epsilon + i\omega')}{z - (\epsilon + i\omega')} . \tag{A3}$$

This last equality follows from the integral

$$\oint_{C'} \frac{d\zeta}{(\zeta - z + \epsilon)(\zeta - i\omega')} = 0 = \mathcal{P} \int_{-\infty}^{\infty} \frac{d\omega}{(i\omega - z + \epsilon)(\omega - \omega')} - \frac{\pi i}{i\omega' - z + \epsilon} , \tag{A4}$$

where the contour $C'$ is along the imaginary axis, excluding the point $i\omega'$, and closes in the left-hand plane, so that all singularities are excluded.

Then writing $\hat{G}(\epsilon + i\omega)$ in (A1) in terms of its real and imaginary parts and using (A3), we find that

$$\hat{G}(z) = \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega \frac{\mathrm{Re}\hat{G}(\epsilon + i\omega)}{z - (\epsilon + i\omega)} , \tag{A5}$$

so that Eq. (3.58) now provides the final step in establishing the desired result, Eq. (3.81).


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# Line Strengths for $Gd^{3+}$ at a $C_{4v}$ Site in $SrF_2$ †

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Oscillator strengths of the transitions from $^8S_{7/2}$ to some of the $^6P$, $^6I$, and $^6D$ multiplets at a $C_{4v}$ symmetry site in $SrF_2$: $Gd^{3+}$ have been measured experimentally and compared with calculations using the Ofelt-Judd theory. Calculations using crystal-field wave functions for the $^6P_{7/2}$ and $^6P_{5/2}$ spectra showed that $J$ mixing is negligible and, in agreement with Zeeman measurements, the transitions are predominantly magnetic dipole. The $^6I$ transitions are predominantly electric dipole and the intensities are in good agreement with theory. The line-strength parameters $T_\lambda$ are $3.4 \pm 0.1$, $1.05 \pm 1.05$, and $12.2 \pm 0.05$ cm $\times 10^{10}$ for $\lambda = 2$, 4, and 6, respectively.

## INTRODUCTION

The alkaline-earth fluorides doped with trivalent rare-earth ions offer a unique opportunity to test line-strength calculations. The cubic site possesses inversion symmetry and allows only magnetic dipole or electric quadrupole transitions. This site is formed when the rare earth, located at a divalent cation site, is charge compensated by a negative ion more than two lattice constants removed.[1] At a site of axial symmetry, which lacks inversion, the odd components in the multipole expansion of the crystal field introduce opposite parity into the states of $f^n$, and electric dipole transitions may occur.

Thus the magnetic dipole strength can be studied independently of the combined electric and magnetic dipole transitions. An analysis of the $^6P$ transitions for the cubic site observed in $CaF_2$:$Gd^{3+}$ has been reported.[2] In this paper the electric dipole contribution observed at a site of $C_{4v}$ symmetry in $SrF_2$:$Gd^{3+}$ is analyzed according to the Ofelt-Judd theory.[3,4]

## OUTLINE OF CALCULATIONS

The calculations will be given in outline form here since the original paper by Judd[4] gives an excellent description of the theory. The contribution to the oscillator strength due to magnetic dipole transitions is given by

$$P_{\mathrm{MD}} = \frac{\pi h}{3mc}\,\frac{n\bar{\nu}}{8}\,\left|\left([^8S_{7/2}]\right|\left|L + g_s S\right|\left|[\alpha LSJ]'\right)\right|^2 .$$

The average energy of the transition is $\bar{\nu}$, $n$ is the index of refraction, and the other constants have a value of $4.028 \times 10^{-8}$ cm. The reduced-matrix elements are given for $\Delta J = 0$ by

$$(\alpha LSJ|\,|L + g_s S|\,|\alpha LSJ) = [J(J+1)]^{1/2} g \ ,$$

where $g$ is the Landé $g$ value given by the formula

$$g = (g_s - 1)\,\frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} + 1 \ .$$

The gyromagnetic ratio of the electron, $g_s$, is 2.00327. For $\Delta J = -1$,