

## Approximants to the nuclear-spin autocorrelation function. Application to $\text{CaF}_2$ <sup>†</sup>

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A simple method for generating approximants to the nuclear-spin autocorrelation function from the known moments is described. Expressions for the two lowest-order approximants are derived and the numerical results are compared with the  $^{19}\text{F}$  experimental free-induction-decay signals in  $\text{CaF}_2$ .

### I. INTRODUCTION

The calculation of the nuclear magnetic resonance (NMR) line shape of a "rigid" lattice of spin- $\frac{1}{2}$  nuclei coupled by magnetic dipole-dipole interactions, is one of the fundamental problems of NMR. Considerable effort has been dedicated to the solution of this problem using a variety of techniques. Early in the history of NMR, Van Vleck<sup>1</sup> calculated the second and fourth moments,  $M_2$  and  $M_4$ , of the absorption line shape. Recently, Jensen and Hansen<sup>2</sup> have produced closed expressions for the sixth and eighth moments,  $M_6$  and  $M_8$ , using a computer to perform the algebraic calculations. Given the enormous amount of computation involved in calculating higher moments, it seems unlikely that exact expressions or values for many higher moments will be produced in the near future. The polynomial expansion of the free-induction-decay signal (fid) converges very slowly, and a large number of moments must be known if a moment expansion is to accurately predict the fid over the first oscillation or two.<sup>3</sup>

A number of approximation techniques have been tried (Refs. 4–8 is a nonexhaustive list) for generating functions with several adjustable parameters, to fit the initial part of the fid. These parameters are chosen so that the function has the correct second, or second and fourth moments. However, the choice of generating functions to fit the fid has been rather arbitrary.

In this paper, we present a different technique for generating functions to fit the fid. It has the advantage of starting with the exact form of the equation of motion for the spin system in the form of a set of difference equations whose coefficients are related to the moments of the line. Solutions to these equations are generated, using an approximation that produces a great mathematical simplification in the equations. The approximation is not physically justifiable but is reasonable and has the advantage of introducing higher-order corrections in an unarbitrary way.

In Sec. II, we give a short derivation of the equations of motion for the correlation function  $G(t)$ . In Sec. III, we find the first approximant

based upon the exact knowledge of  $M_2$ , and the second approximant based upon exact knowledge of  $M_2$  and  $M_4$ . Even the first approximant displays the damped oscillations that are experimentally observed in solids. The second approximant is compared with recent measurements<sup>9</sup> of the  $^{19}\text{F}$  fid signals in  $\text{CaF}_2$ .

### II. EQUATIONS OF MOTION

The quantity of interest in a pulsed NMR experiment, where the system of spins is prepared by a  $\frac{1}{2}\pi$  pulse in a state described at  $t=0$  by a density matrix  $\sigma(0) = \text{const } I_x$ , is the spin autocorrelation function given by<sup>8</sup>

$$G(t) = \text{Tr}(I_x(t)I_x) / \text{Tr}(I_x^2), \quad (1)$$

where

$$I_x(t) = e^{i\mathcal{H}t/\hbar} I_x e^{-i\mathcal{H}t/\hbar}. \quad (2)$$

A large external field is assumed to be applied along the  $z$  axis. The Hamiltonian  $\mathcal{H}$  in Eq. (2) is then the truncated magnetic dipole-dipole interaction energy.<sup>8</sup>

Equations (1) and (2) are the starting point for many calculations<sup>3,10–12</sup> of the fid signal  $G(t)$  or its Fourier transform  $g(\omega)$ , the absorption spectrum. Several operator expansion techniques have been used in connection with the calculation of the spin autocorrelation function defined by Eq. (1).

For our purposes, however, a different approach will be followed. Defining the Liouville operator  $\mathcal{L}$  as

$$\mathcal{L} = (1/\hbar)[\mathcal{H}, \quad ], \quad (3)$$

Eq. (2) can be written as

$$I_x(t) = e^{it\mathcal{L}} I_x. \quad (4)$$

An expansion of the exponential operator in Eq. (4) yields

$$I_x(t) = \sum_{j=0}^{\infty} \frac{(it)^j}{j!} \mathcal{L}^j I_x. \quad (5)$$

If both sides of Eq. (5) are multiplied by  $I_x$  and then the trace is taken, one obtains the usual moment expansion of the autocorrelation function.

We will now follow Lado, Memory, and Parker<sup>13</sup> and consider the operators  $\mathcal{L}^j I_x$  as a complete set of vectors  $|\mathcal{L}^j I_x\rangle$  in a Hilbert space of operators defined for the system. In this Hilbert space of operators, the inner product of two arbitrary vectors  $A$ ,  $B$  is defined as

$$(A|B) = \text{Tr}(A^\dagger B) = (B|A)^* , \quad (6)$$

where  $A^\dagger$  is the Hermitian adjoint of the vector  $A$ . It is convenient to construct from the complete set  $|\mathcal{L}^j I_x\rangle$  an orthogonal set  $|j\rangle$  using the Schmidt process.<sup>14</sup> In terms of the orthogonal vectors,  $|j\rangle$ ,  $I_x(t)$  in Eq. (5) is given by

$$|I_x(t)\rangle = \sum_{j=0}^{\infty} A_j(t) |j\rangle . \quad (7)$$

Since the vector  $|0\rangle$  of the orthogonal set is identical to the vector  $|I_x\rangle$  of the original set, the coefficient  $A_0(t)$  can readily be seen to be equal to the free-induction-decay signal  $G(t)$ .

$$A_0(t) = \frac{(0|I_x(t))}{(0|0)} = \frac{\text{Tr}(I_x(t)I_x)}{\text{Tr}(I_x^2)} = G(t) \quad (8)$$

The coefficients  $A_j(t)$  with  $j \geq 1$  involve rather complicated traces and need not be explicitly considered here.

For a Hamiltonian involving magnetic dipole-dipole interactions, all odd-valued moments vanish.<sup>8</sup> It is shown in Ref. 13 that under these circumstances, the coefficients  $A_j(t)$  satisfy the following simple equations of motion:

$$\begin{aligned} -i\dot{A}_0 &= \nu_0^2 A_1 , \\ -i\dot{A}_1 &= A_0 + \nu_1^2 A_2 , \\ -i\dot{A}_2 &= A_1 + \nu_2^2 A_3 , \\ &\vdots \\ -i\dot{A}_n &= A_{n-1} + \nu_n^2 A_{n+1} , \\ &\vdots \end{aligned} \quad (9a)$$

with the initial conditions

$$A_0(0) = 1, \quad A_j(0) = 0, \quad j \geq 1 . \quad (9b)$$

The parameters  $\nu_j^2$  are related to the moments  $M_k$  of the absorption line and are given by<sup>15</sup>

$$\nu_j^2 = D_{j-1} D_{j+1} / D_j^2 . \quad (10)$$

$D_j$  is a determinant of the form

$$D_j = \begin{vmatrix} 1 & M_1 & \cdots & M_j \\ M_1 & M_2 & \cdots & M_{j+1} \\ \vdots & \vdots & \ddots & \vdots \\ M_j & M_{j+1} & \cdots & M_{2j} \end{vmatrix} , \quad (11a)$$

where only even-valued moments  $M_n$  are different from zero. The first few  $D$ 's and  $\nu$ 's are

$$\begin{aligned} D_1 &= D_0 = 1, \quad D_2 = M_2, \quad D_3 = M_2(M_4 - M_2^2), \\ D_4 &= (M_4 - M_2^2)(M_2 M_6 - M_4^2), \\ \nu_0^2 &= M_2, \quad \nu_1^2 = \frac{M_4 - M_2^2}{M_2}, \quad \nu_2^2 = \frac{M_2 M_6 - M_4^2}{M_2(M_4 - M_2^2)}. \end{aligned} \quad (11b)$$

The calculation of the fid signal  $G(t)$  is equivalent to solving for  $A_0(t)$  in the infinite set of first-order coupled linear differential equations [Eqs. (9)]. Normally, only a few of the parameters  $\nu_j^2$  are known in practice and some approximations are necessary in order to obtain a definite answer for  $A_0(t)$ .

From Eqs. (9a), it can be seen that if for some particular value of  $k$ ,  $\nu_k^2 = 0$ , then the autocorrelation function  $A_0(t)$  becomes independent of all  $\nu_j^2$ 's with  $j \geq k$ . The values of only the 2nd, 4th, ...,  $2k$ th moments are then necessary to determine the line shape. The simplest example of such a case is provided by a system of isolated pairs of spin- $\frac{1}{2}$  nuclei in an external magnetic field, interacting via their magnetic dipole moments. An application of Van Vleck's<sup>1</sup> formulas for this case yields  $\nu_1^2 = 0$ , and the solutions to Eqs. (9) become  $A_0(t) = \cos(\sqrt{M_2}t)$ , which is the exact solution for the autocorrelation function.<sup>16</sup>

Similarly, for a collection of spin- $\frac{1}{2}$  nuclei arranged in the form of isolated equilateral triangles in an external magnetic field perpendicular to the plane of the triangle,<sup>17</sup> the autocorrelation function has the form  $A_0(t) = \frac{1}{2}[1 + \cos(\sqrt{2M_2}t)]$ . It is easy to verify that, in this case,  $\nu_2^2 = 0$ .

In the general one-, two-, or three-dimensional cases, the spins cannot be conveniently paired for computing  $G(t)$ , and one thus expects that all  $\nu_j^2$  are different from zero. The calculation of  $A_0(t)$  does not reduce to the solution of a finite system of coupled differential equations with only a finite number of frequencies. We will now make the assumption that all the  $\nu_j$ 's are nonzero. For this case, it will be convenient but not necessary to transform the  $A_j$ 's and  $\nu_j^2$ 's in Eq. (9) in the following manner:

$$\tau_{2n}^{-1} \equiv \left( \frac{\nu_{2n-1}^2 \nu_{2n-3}^2 \cdots \nu_1^2}{\nu_{2n-2}^2 \nu_{2n-4}^2 \cdots \nu_0^2} \right) |\nu_0| , \quad n = 1, 2, 3, \dots \quad (12)$$

$$\tau_{2n+1}^{-1} \equiv \left( \frac{\nu_{2n}^2 \nu_{2n-2}^2 \cdots \nu_2^2}{\nu_{2n-1}^2 \nu_{2n-3}^2 \cdots \nu_1^2} \right) |\nu_0| , \quad I_{2n} \equiv (-i)^{2n} \nu_{2n-1}^2 \nu_{2n-3}^2 \cdots \nu_1^2 A_{2n} , \quad n = 1, 2, 3, \dots \quad (13)$$

$$I_{2n+1} \equiv (-i)^{2n+1} \nu_{2n}^2 \nu_{2n-2}^2 \cdots \nu_2^2 |\nu_0| A_{2n+1} ,$$

With

$$\tau_0^{-1} = \tau_1^{-1} = |\nu_0| = \sqrt{M_2}, \quad I_0 \equiv A_0, \quad I_1 \equiv -i|\nu_0| A_1 .$$

With these definitions, Eqs. (9) can be written in

a more compact form as

$$\begin{aligned} \dot{I}_0 &= -(1/\tau_0)I_1, \\ \dot{I}_1 &= (1/\tau_1)(I_0 - I_2), \\ &\vdots \\ \dot{I}_n &= (1/\tau_n)(I_{n-1} - I_{n+1}), \\ &\vdots \end{aligned} \quad (14)$$

with

$$I_0(0) = 1, \quad I_n(0) = 0, \quad n \geq 1. \quad (15a)$$

The first few  $\tau$ 's are given by

$$\begin{aligned} \tau_0^{-1} &= \sqrt{M_2} = \tau_1^{-1}, \\ \tau_2^{-1} &= [(M_4 - M_2^2)/M_2^2] M_2^{1/2}, \\ \tau_3^{-1} &= \{(M_2 M_6 - M_4^2)/[(M_4 - M_2^2)^2]\} M_2^{1/2}. \end{aligned} \quad (15b)$$

Let  $\bar{I}_n(S)$ , defined by

$$\bar{I}_n(S) = \int_0^\infty e^{-St} I_n(t) dt, \quad 0 \leq S, \quad (16)$$

be the Laplace transform of  $I_n(t)$ . Then, taking into account the initial conditions listed in Eq. (15), Eq. (14) can be transformed into the following form:

$$\begin{aligned} S\bar{I}_0 &= 1 - (1/\tau_0)\bar{I}_1, \\ S\bar{I}_1 &= (1/\tau_1)(\bar{I}_0 - \bar{I}_2), \\ &\vdots \\ S\bar{I}_n &= (1/\tau_n)(\bar{I}_{n-1} - \bar{I}_{n+1}). \end{aligned} \quad (17)$$

Because of the initial conditions on  $I_n(t)$ , the initial value theorem yields the following properties of  $\bar{I}_n(S)$ :

$$\lim_{S \rightarrow \infty} S\bar{I}_0(S) = 1, \quad \lim_{S \rightarrow \infty} S\bar{I}_n(S) = 0, \quad n \geq 1. \quad (18)$$

### III. SOLUTION OF THE EQUATION OF MOTION

A formal solution to find  $\bar{I}_0(S)$  is easy to carry out if one knows all of the  $\tau_n$ 's (which one does not). We have thus looked for a judicious approximation to make here, and we have tried to introduce a certain amount of physical intuition. Equation (14) resembles the equations for a lumped-element-transmission line<sup>18</sup> (however, with negative resistances and inductances), and we have chosen to view it as such. For such a model,  $I_0(t)$  can be viewed as the current in the zeroth loop. Because of the finite propagation speed of signals, the short-time behavior of  $I_0(t)$  is mainly determined by the parameters  $\tau_j$  describing the loops immediately adjacent to the zeroth loop. The  $\tau_n$ 's for the far away loops are unknown but also are not as important as the near loops in determining the short-time behavior of  $I_0(t)$ . For the far away

loops, we assume all the unknown  $\tau_n$ 's are equal to the last known  $\tau_p$ . Then Eq. (17) becomes

$$\begin{aligned} \tau_0 S\bar{I}_0 + \bar{I}_1 &= \tau_0, \\ -\bar{I}_0 + S\tau_1\bar{I}_1 + \bar{I}_2 &= 0, \\ -\bar{I}_1 + S\tau_2\bar{I}_2 + \bar{I}_3 &= 0, \\ &\vdots \\ -\bar{I}_{n-1} + S\tau_n\bar{I}_n + \bar{I}_{n+1} &= 0, \quad 1 \leq n \leq p, \end{aligned} \quad (19)$$

$$-\bar{I}_{n-1} + S\tau_p\bar{I}_n + \bar{I}_{n+1} = 0, \quad p \leq n. \quad (20)$$

The above infinite set of equations for  $p \leq n$  can be solved by using the difference operator<sup>19</sup>  $E$  defined as

$$E\bar{I}_n(S) = \bar{I}_{n+1}(S). \quad (21)$$

In terms of  $E$ , Eq. (20) can be rewritten as

$$(-E^{-1} + S\tau_p + E)\bar{I}_n = 0, \quad p \leq n. \quad (22)$$

Since  $\bar{I}_n(S)$  is different from zero for some values of  $S$  and  $n$ , then

$$E + S\tau_p - E^{-1} = 0, \quad (23)$$

which is satisfied by

$$E = \lambda_\pm = -\frac{1}{2}S\tau_p \pm [1 + (\frac{1}{2}S\tau_p)^2]^{1/2}. \quad (24)$$

Thus the general solution is

$$\bar{I}_n(S) = C_+ \lambda_+^n + C_- \lambda_-^n, \quad p \leq n, \quad (25)$$

where the constants  $C_+$  and  $C_-$  are chosen to satisfy boundary conditions. For  $\frac{1}{2}S\tau_p \gg 1$ ,

$$\lambda_+ \approx (S\tau_p)^{-1}, \quad \lambda_- = -(S\tau_p), \quad (26)$$

$$\bar{I}_n(S) \approx C_+ \tau_p^n S^{-n} + C_- (-\tau_p)^n S^n. \quad (27)$$

The second term in Eq. (27) goes to infinity when  $\lim_{S \rightarrow \infty} S\bar{I}_n(S)$  is taken, thus violating Eq. (18). We thus have to set  $C_- = 0$ , and  $C_+$  must be different from zero to have a nontrivial solution. Then,

$$\bar{I}_{n+1}/\bar{I}_n = \bar{I}_{p+1}/\bar{I}_p = \lambda_+, \quad p \leq n, \quad (28)$$

and Eq. (19) can be rewritten as

$$\begin{aligned} \tau_0 S\bar{I}_0 + \bar{I}_1 &= \tau_0, \quad -\bar{I}_0 + S\tau_1\bar{I}_1 + \bar{I}_2 = 0, \\ -\bar{I}_1 + S\tau_2\bar{I}_2 + \bar{I}_3 &= 0, \\ &\vdots \\ -\bar{I}_{p-2} + S\tau_{p-1}\bar{I}_{p-1} + \bar{I}_p &= 0, \\ -\bar{I}_{p-1} + (S\tau_p + \lambda_+)\bar{I}_p &= 0. \end{aligned} \quad (29)$$

This set of equations can be solved for  $\bar{I}_0$  using Cramers rules.

#### A. Case of $p=1$

The simplest case to solve is where  $p=1$ , and thus all  $\tau_n = \tau_0$ . Then Eq. (29) reduces to

$$\tau_0 S\bar{I}_0 + \bar{I}_1 = \tau_0, \quad -\bar{I}_0 + (S\tau_0 + \lambda_+)\bar{I}_1 = 0. \quad (30)$$

Solving for  $\bar{I}_0(S)$  and simplifying the results yields

$$\bar{I}_0(S) = \frac{1}{2} \tau_0^2 \{-S + [S^2 + (2/\tau_0)^2]^{1/2}\}. \quad (31)$$

The inverse transform of  $\bar{I}_0(S)$  can be found in a table.<sup>20</sup> The result is

$$I_0(t) = J_1(2(M_2)^{1/2}t)/(M_2)^{1/2}t = G^{(1)}(t), \quad (32)$$

where  $G^{(1)}(t)$  is the first-order approximant to the desired autocorrelation function, and  $J_1$  is a Bessel function of order 1.

Since  $G^{(1)}(t)$  and  $G(t)$  both have values of 1 for  $t=0$  and the same second moment, so  $G^{(1)}(t)$  is a good approximation to  $G(t)$  for short times, as is to be expected. For the case of the  $^{19}\text{F}$  fid in  $\text{CaF}_2$ ,  $G^{(1)}(t)$  seems to approximate  $G(t)$  reasonably well to about the time  $t_1$  of the first zero value of  $G(t)$ , as can be seen from Table I. Both  $G^{(1)}(t)$  and the  $G(t)$  for  $\text{CaF}_2$  have an infinite number of zeros for which the time between the zeros tend to approach a limit from above for increasing  $t$ , but the values are not too close. Another important difference in the long-time region is that the envelope of  $G^{(1)}(t)$  goes to zero as  $t^{-3/2}$ , while for  $\text{CaF}_2$ , it is experimentally found that the envelope of  $G(t)$  goes to zero as  $e^{-t}$ .

#### B. Case of $p=2$

The second approximant is found by setting  $p=2$ , which implies all  $\tau_n = \tau_2$  for  $2 \leq n$ . Then Eq. (29) reduces to

$$\begin{aligned} \tau_0 S \bar{I}_0 + \bar{I}_1 &= \tau_0, & -\bar{I}_0 + S \tau_0 \bar{I}_1 + \bar{I}_2 &= 0, \\ -\bar{I}_1 + (S \tau_2 + \lambda_+) \bar{I}_2 &= 0. \end{aligned} \quad (33)$$

Solving for  $\bar{I}_0$  and simplifying the results yields

$$\bar{I}_0(S) = \tau_0 \left( \frac{S \tau_0 + \lambda_+}{1 + S \tau_0 (S \tau_0 + \lambda_+)} \right). \quad (34)$$

This expression for  $\bar{I}_0(S)$  is more complicated than the first case, and we must take the inverse Laplace transform of Eq. (34) to find the second approximant  $G^{(2)}(t)$ ,

$$I_0(t) = G^{(2)}(t) = \frac{1}{2\pi i} \int_{\gamma-i\infty}^{\gamma+i\infty} e^{St} \bar{I}_0(S) dS. \quad (35)$$

TABLE I. Time of occurrence of the first zero  $t_1$  of the  $^{19}\text{F}$  free-induction-decay signal in  $\text{CaF}_2$  at 4.2 K.

Direction of $\vec{B}_0$	$t_1$ ( $\mu\text{sec}$ ) Experimental <sup>a</sup>	$t_1$ ( $\mu\text{sec}$ ) Theoretical <sup>b</sup>
[100]	21.38 $\pm$ 0.01	21.1
[111]	55.22 $\pm$ 0.08	50.5
[110]	37.07 $\pm$ 0.05	34.7

<sup>a</sup>Taken from Ref. 9.

<sup>b</sup>Computed from Eq. (32) using experimental  $M_2^{1/2}$  values of Ref. 9.

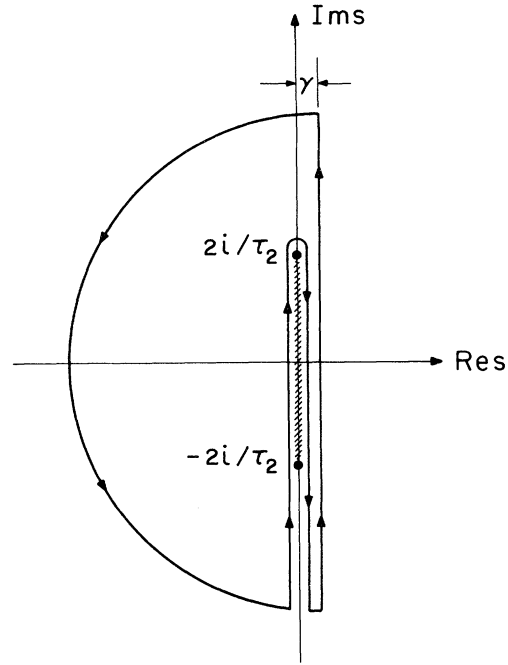


FIG. 1. Path of integration for the inverse Laplace transformation indicated by Eq. (35).

By setting the denominator in Eq. (34) equal to zero, we find it has four roots  $S_1, S_2, S_3,$  and  $S_4$ .

$$\begin{aligned} S_1 = -S_3 &= \frac{1}{\tau_0} \left\{ \frac{1}{2} \left[ -1 + i \left( \frac{3+\alpha}{1-\alpha} \right)^{1/2} \right] \right\}^{1/2}, \\ S_2 = -S_4 &= \frac{1}{\tau_0} \left\{ \frac{1}{2} \left[ -1 - i \left( \frac{3+\alpha}{1-\alpha} \right)^{1/2} \right] \right\}^{1/2}, \end{aligned} \quad (36)$$

$$\alpha = \frac{\tau_2}{\tau_0} = \left( \frac{M_4}{M_2^2} - 1 \right)^{-1}.$$

For the applied magnetic field  $\vec{B}_0$  along the [100], [110], and [111] crystal axes of a  $\text{CaF}_2$  crystal,  $M_4 > 2M_2^2$ . For this case,  $\alpha < 1$  and  $(3+\alpha)/(1-\alpha)$  is positive. The integral in Eq. (35) for  $G^{(2)}(t)$  lies on the first sheet of the Riemann surface defined for the function  $\bar{I}_0(S)$  which contains a square-root function. With a little work it can be shown that  $S_1, S_2, S_3,$  and  $S_4$  all lie on the second sheet. Thus, as long as we carry out any contour integrations on the first sheet only, we will not enclose any poles of  $\bar{I}_0(S)$ . The path of integration for the integral in Eq. (35) is closed in a large semicircle, as indicated in Fig. 1, and we use Eq. (34) to analytically continue  $\bar{I}_0(S)$  for  $\text{Re}S < 0$ . Since no poles are enclosed, the only contribution to the integral comes from the part along the branch cut shown in Fig. 1.

The final result for the second-order approxi-

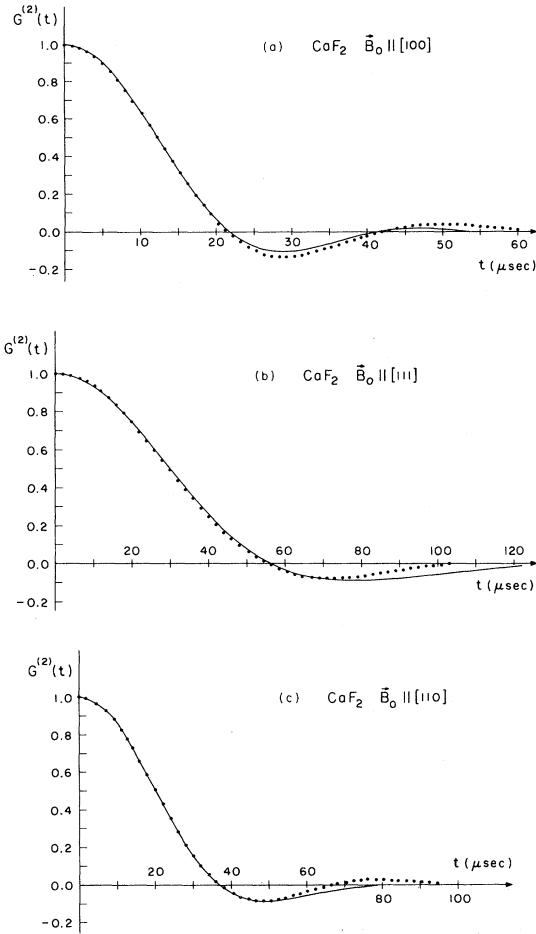


FIG. 2. Comparison of the second-order approximants  $G^{(2)}(t)$  to the autocorrelation function. Solid lines represent the calculated values of  $G^{(2)}(t)$  from Eq. (37) using experimental  $M_2$  and  $M_4$  values from Ref. 9. Dots are the experimental fid signals for  $^{19}\text{F}$  in  $\text{CaF}_2$  at 4.2 K for three different orientations, relative to the crystal axes, of the applied magnetic field. (a)  $\vec{B}_0 \parallel [100]$ , (b)  $\vec{B}_0 \parallel [111]$ , (c)  $\vec{B}_0 \parallel [110]$ .

mant  $G^{(2)}(t)$  to the desired autocorrelation function is

$$G^{(2)}(t) = \int_{-2/\tau_2}^{2/\tau_2} g^{(2)}(\omega) \cos(\omega t) d\omega, \quad (37)$$

where

$$g^{(2)}(\omega) = \frac{1}{\pi \tau_0^2 (\tau_0 - \tau_2)} \frac{(1 - \frac{1}{4} \tau_2^2 \omega^2)^{1/2}}{(\omega^2 - \omega_+^2)(\omega^2 - \omega_-^2)},$$

$$\text{for } -\frac{2}{\tau_2} \leq \omega \leq \frac{2}{\tau_2}, \quad (38a)$$

$$g^{(2)}(\omega) = 0, \quad \text{for } \frac{2}{\tau_3} < |\omega|, \quad (38b)$$

$$\omega_{\pm}^2 = \frac{1}{2\tau_0^2} \left[ 1 \pm i \left( \frac{3 + \alpha}{1 - \sigma} \right)^{1/2} \right]. \quad (39)$$

$\tau_0$  and  $\tau_2$  are defined in Eq. (15b), and  $\alpha$  is defined in Eq. (36). We have obtained in Eqs. (38) and (39) a simple closed expression for  $g^{(2)}(\omega)$ , the absorption spectrum corresponding to  $G^{(2)}(t)$ .

The case of  $p=1$  can be reproduced by setting  $\tau_2 = \tau_0$ , thus providing a check on the consistency of the results. The expression for  $g^{(2)}(\omega)$  simplifies greatly, and the integral of Eq. (37) can be evaluated in closed form, yielding the same result as Eq. (32). That is,  $G^{(2)}(t)$  reduces for this special case to the first-order approximant  $G^{(1)}(t)$  as it should. When  $\tau_2 \neq \tau_0$ , the evaluation of Eq. (37) in closed form is more difficult. Using the experimental  $M_2$  and  $M_4$  values<sup>9</sup> for the  $^{19}\text{F}$  fid signals in  $\text{CaF}_2$  at 4.2 K, we have carried out the Fourier transform of  $g^{(2)}(\omega)$  by numerical integration of Eq. (37). The results are shown in Fig. 2 for the applied field  $B_0$  along the [100], [110], and [111] crystal axes, along with the experimental fid's from Ref. 9.

The agreement of  $G^{(2)}(t)$  with the experimental fid's is extremely good from the origin to the minimum following the first crossing point. While  $G^{(2)}(t)$  is not a good approximation past that point, it is a well-behaved function that does not diverge for long times. All of the approximants display the damped oscillatory characteristics of the autocorrelation function, the damping being slower than what is observed in the experimental fid signals. A more sophisticated guess as to the dependence of  $\tau_n$  upon  $n$  could probably improve this part of the result considerably. However, in view of the extremely simplified formulation of the problem implicit in the equations of motion listed in Eq. (29) and the minimum amount of numerical computation involved in solving them, the results are rewarding. Further, the procedure can be easily and systematically generalized to include higher moments.

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