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Expansion Theorems for Magnetic-Resonance Line Shapes

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We have found an exact expression or expansion theorem for a free-induction-decay (FID) curve which involves all the moments of the corresponding cw absorption line as well as two arbitrary scale factors or parameters which may be chosen to optimize the convergence which is necessarily uniform. The expression obtained is a generalization of Taylor's theorem known as a Newmann expansion, and it gives an FID curve as either an exponential or Gaussian damping factor times an infinite series of Bessel functions which may describe the oscillations characteristic of certain FID shapes. Any one of the (infinitely) many Bessel-function expansions may be used to represent a particular FID curve, although there will be one which requires the fewest terms for a specified accuracy of approximation. Application of these expansions to FID curves from calcium fluoride shows that it is possible to obtain an excellent fit to the data, using only the theoretical second and fourth moments for the expansion whose leading term corresponds to Abragam's trial function. Furthermore, when several exact but different expansions were truncated to only three terms it was found that they were nearly equal to each other and to the data over a major portion of the decay for the optimum choice of the two scale factors. Another application of these expansions would be the determination of the moments of a given FID curve, using the orthogonality integral for Bessel functions.

I. INTRODUCTION

The problem of calculating the shape of magnetic resonance absorption lines was first discussed by Van Vleck[1] who showed that the moments of the line could be calculated exactly. The $2n$th moment of a normalized line-shape function $G(\omega)$ is given by

$$M_{2n}=\int_0^\infty \omega^{2n}G(\omega)\,d\omega,$$

where

$$\int_0^\infty G(\omega)\,d\omega=1$$

and $\omega=0$ corresponds to the center of the line. Since $G(\omega)$ is symmetric about its center, the odd moments are zero. The second and fourth moments were evaluated by Van Vleck[1] for a system of spins on a lattice with dipole-dipole and exchange interactions and were found to agree with experimental measurements on calcium fluoride.[2,3] An important result of these calculations was that a quantitative theoretical test was provided to determine the degree of Gaussian or Lorentzian character of an absorption line, these shapes being characteristic of magnetic resonance lines in general.[2,4] Thus, for example, the resonance line shape(s) from calcium fluoride could be shown to deviate somewhat from the Gaussian shape predicted by the local-field model of Bloembergen, Purcell, and Pound.[4]

Further development in the theory was made by Lowe and Norberg[5] who showed that a line-shape function $G(\omega)$ was the Fourier transform of the corresponding free-induction-decay (FID) function $F(t)$ which represents the amplitude of the magnetization following a 90° rf pulse. Consequently,

$$F(t)=\int_0^\infty \cos(\omega t)\,G(\omega)\,d\omega,$$

and, therefore,

$$F(t)=\sum_{n=0}^{\infty}(-1)^n M_{2n}\frac{t^{2n}}{(2n)!}\quad. \tag{1}$$

This expansion theorem gives an exact expression for the line shape in terms of Van Vleck's moments, although many terms are required to fit an experimental FID curve.

More recently, Lee, Tse, Goldburg, and Lowe[6] and independently Evans and Powles[7] showed by iteration of an equation of motion for the magnetization that the FID function could be written as

$$F(t)=F_0(t)+F_1(t)+F_2(t)+\cdots, \tag{2}$$

where each term is explicitly defined as a trace of a certain operator obtained from Van Vleck's Hamiltonian. Only the first two terms of this series have been evaluated exactly,[7-10] however, although an approximation to F_2 has been determined.[10,11] Higher terms in (2) have not been studied because of their complexity.

An alternative to (1) or (2) was proposed by Abragam[12] who suggested the trial function

$$F(t) = e^{-\alpha^2 t^2} \sin(\beta t)/\beta t \tag{3}$$

for FID curves from crystals with a single dipolar-broadened resonance line such as calcium fluoride. The function (3) gives excellent agreement with the data of Bruce[3] and Lowe and Norberg[5] from calcium fluoride when the constants α and β are determined from the theoretical M_2 and M_4, so that (3) matches the first three terms of (1).[12]

We have found that (3) is the first term of an exact expansion for $F(t)$ in terms of the moments,

$$F(t) = e^{-\alpha^2 t^2} \sum_{n=0}^{\infty} a_{2n} j_{2n}(\beta t), \tag{4}$$

where the j_{2n} are spherical Bessel functions $a_0 = 1$, and the other coefficients are constants depending on the moments and the (arbitrary) choice made for the scale factors α and β. It is therefore possible to determine $F(t)$ theoretically to any desired accuracy using (4) rather than (1). In fact, (4) represents a generalization of (1). In practice this expansion will be useful when only a small number of terms are required. Already for calcium fluoride the first term is an excellent approximation for Abragam's choice of α and β.[12] For other FID shapes this would not be the case. However, we will show in Sec. II that many other expansions of the type (4) can be determined so that it may be possible to find one whose leading term is a satisfactory approximation for a particular $F(t)$. Of course, each of these expansions, for a given set of realistic moments, will converge uniformly to the same function so that the choice of expansion is immaterial, provided enough moments are known. Two advantages of using an expansion such as (4) rather than (2) are, first, that the moments are more easily evaluated than the terms of (2) and, second, that the FID function for a powder sample may be evaluated by averaging the moments themselves rather than performing a numerical integration of the terms in (2). In addition, the convergence properties of (4) are known.

In Sec. II we develop general formulas for expansion theorems having a damping factor of $\exp(-\alpha^2 t^2)$ or $\exp(-\alpha t)$ times a series of Bessel functions of various orders which can describe the oscillations characteristic of certain FID curves. In Sec. III we apply several different expansions to the dipolar-broadened resonance line observed in calcium fluoride.

II. EXPANSION THEOREMS

We will consider the FID function to be defined by its power series (1) for both positive and negative t. For any realistic system this series must converge for all finite t, and hence, when considered as a function of a complex variable t, it must represent an entire function.[13] In the rest of this section the variable t will be considered as complex.

Let $f(z)$ be an arbitrary entire function of the complex variable z. Applying Cauchy's formula,[14] we obtain

$$f(z) = (1/2\pi i) \int_C [f(t)/(t-z)]\, dt, \tag{5}$$

where C is taken to be a circle about the origin in the positive sense enclosing the point z so that $|z| < |t|$. Since $f(z)$ is entire, the radius of C in (5) can be any finite value so that if $(t-z)^{-1}$ is expanded in powers of z/t we will obtain Taylor's expansion[15] about $z = 0$, which will be valid for all finite z. Neumann has shown that an alternative expansion exists, namely,

$$(t-z)^{-1} = \sum_{n=0}^{\infty} \epsilon_n A_n(t) J_n(z), \tag{6}$$

where this expansion is valid when $|t| > |z|$ and converges uniformly in both t and z for t and z in their respective domains.[16] The $J_n(z)$ are Bessel functions of order n, $A_n(t)$ are Neumann polynomials, $\epsilon_0 = 1$, and otherwise $\epsilon_n = 2$. Using (5) and (6), we obtain

$$f(z) = \sum_{n=0}^{\infty} a_n J_n(z),$$

where

$$a_n = (\epsilon_n/2\pi i) \int_C f(t) A_n(t)\, dt.$$

Now the $A_n(t)$ are given by[16]

$$A_0 = 1/t,$$

$$A_n = \frac{1}{4} \sum_{m=0}^{\leqq n/2} \frac{n(n-m-1)!}{m!\,(\frac{1}{2}t)^{n-2m+1}}, \quad n \geqq 1.$$

To evaluate the a_n we need only determine the residue of $f(t)A_n(t)$ at $t = 0$. Using the Taylor expansion of $f(t)$ about $t = 0$ and $A_n(t)$, we may write $f(t)A_n(t) = R_n/t + \cdots$, where R_n is the residue desired. We obtain, finally, $a_n = \epsilon_n R_n$, where

$$a_0 = f^{(0)}(0),$$

$$A_n = 2 \sum_{l=0,1}^{n}{}' \frac{2^l n}{n+l} \binom{\frac{1}{2}(n+l)}{l} f^{(l)}(0), \quad n \geqq 1.$$

The sum is restricted to either even or odd l where

$l = 0, 2, 4, \ldots, n$ if n is even and $l = 1, 3, 5, \ldots, n$ if n is odd. The $f^{(l)}(0)$ represent the derivatives of $f(t)$ at $t = 0$, and

$$\binom{n}{m}$$

is the binomial coefficient. For example, if $f(z) = 1$ we have

$$f^{(0)}(0) = 1, \quad f^{(l)}(0) = 0 \quad \text{for} \quad l \geqq 1,$$

$$a_0 = 1, \qquad a_n = 2 \quad \text{for } n \text{ even},$$

$$a_n = 0 \qquad \text{for } n \text{ odd}.$$

for n odd. Thus, we obtain

$$1 = J_0 + 2J_1 + 2J_2 + \cdots.$$

For fitting FID curves it is convenient to introduce an arbitrary scale factor β so that

$$f(z) = \sum_{n=0}^{\infty} a_n J_n(\beta z).$$

The effect on the coefficients is to introduce a factor $1/\beta^l$ in (7), as can be deduced from scaling (6). The result is

$$a_0 = f^{(0)}(0), \qquad a_n = \sum_{l=0,1}^{\infty}{}' \frac{2^l n}{n+l} \binom{\frac{1}{2}(n+l)}{l} \frac{f^{(l)}(0)}{\beta^l}. \tag{7}$$

We now choose $f(z) = e^{\alpha z} F(z)$ and $f(z) = e^{\alpha^2 z^2} F(z)$ where $F(z)$ is the FID function. Since $F(z)$, $\exp(\alpha z)$, and $\exp(\alpha^2 z^2)$ are entire functions of z so are their products, and we have the following expansions which are valid for all finite z:

$$F(z) = e^{-\alpha z} \sum_{n=0}^{\infty} a_n J_n(\beta z), \qquad F(z) = e^{-\alpha^2 z^2} \sum_{n=0}^{\infty} a_n J_n(\beta z), \tag{8}$$

where the coefficients are given by (7).

There is an expansion more general than (8) which is due to Gegenbauer. It is obtained from the expansion[16]

$$z^{\nu}(t-z)^{-1} = \sum_{n=0}^{\infty} A_{n,\nu}(t) J_{n+\nu}(z),$$

where $|t| > |z|$, $\nu \neq -1, -2, \ldots,$ and the A_n are Gegenbauer polynomials

$$A_{n,\nu} = \frac{2^{\nu+n}(\nu+n)}{t^{n+1}} \sum_{m=0}^{\leqq n/2} \frac{\Gamma(\nu+n-m)}{m!} \left(\tfrac{1}{2}t\right)^{2m},$$

where $\Gamma(z)$ is the γ function and for $n = \nu = 0$, $A_{0,0} \equiv 1/t$. Introducing a scale factor β and proceeding as before, we obtain

$$f(z) = \sum_{n=0}^{\infty} b_n J_{n+\nu}(\beta z)/(\beta z)^{\nu},$$

where

$$b_n = \sum_{l=0,1}^{n}{}' (\nu+n)\, 2^{\nu+l} \frac{\Gamma[\nu + \frac{1}{2}(n+l)]}{l!\,[\frac{1}{2}(n-l)]!} \frac{f^{(l)}(0)}{\beta^l}, \tag{9}$$

where ν is not a negative integer and the sum is restricted to l even (odd) for n even (odd). It may be verified that b_n given by (9) reduces to a_n as given by (7) when $\nu = 0$ [for $\nu = 0$ and $n = 0$, we require the convention that $n\Gamma(n) = n! = 1$ for $n = 0$]. Thus, as before, we may expand the FID function using

$$F(z) = e^{-\alpha z} \sum_{n=0}^{\infty} \frac{b_n J_{n+\nu}(\beta z)}{(\beta z)^{\nu}}, \qquad F(z) = e^{-\alpha^2 z^2} \sum_{n=0}^{\infty} \frac{b_n J_{n+\nu}(\beta z)}{(\beta z)^{\nu}}, \tag{10}$$

where these expansions are valid for all finite z since $F(z)$ is entire.

In order to apply (10) we need $f^{(l)}(0)$ where we have chosen the two forms $f(z) = \exp(\alpha z) F(z)$ and $f(z) = \exp(\alpha^2 z^2) F(z)$. By definition

$$F(z) = \sum_{n=0}^{\infty} (-1)^n M_{2n} z^{2n}/(2n)!,$$

so that

$$F^{(2n)}(0) = (-1)^n M_{2n}.$$

For $f(z) = H(z) F(z)$ we have

$$f^{(l)}(0) = \sum_{m=0}^{l} \binom{l}{m} H^{(l-m)}(0)\, F^{(m)}(0),$$

where $H^{(k)}(0)$ is the kth derivative of $\exp(\alpha z)$ or $\exp(\alpha^2 z^2)$ evaluated at $z = 0$. Evaluating these derivatives, we have for the exponential case

$$f^{(l)}(0) = \sum_{m=0}^{\leqq l/2} \binom{l}{m} (-1)^m M_{2n} \alpha^{l-2m}, \tag{11}$$

and for the Gaussian case only even derivatives which are given by

$$f^{(2l)}(0) = \pi^{-1/2} \sum_{m=0}^{l} \binom{2n}{2m} (-1)^m M_{2m} \times \Gamma(\tfrac{1}{2} + l - m)(4\alpha^2)^{l-m}. \tag{12}$$

Thus, using (9)–(12), we may calculate any FID curve for a resonance line whose moments are known. Optimum choices for α and β will be discussed in Sec. III, where these formulas are applied to line shapes from calcium fluoride.

Two general remarks can be made concerning the use of (8) or (10). Consider, for example, the expansion (8) with Gaussian prefactor which will contain only even-order Bessel functions as follows from (7) and (12),

$$F(t) = e^{-\alpha^2 t^2} \sum_{n=0}^{\infty} a_{2n} J_{2n}(\beta t). \tag{13}$$

It also follows that $a_0 = 1$ and $a_{2n} = 2 + \Delta a_{2n}$ for $n \geqq 1$. Thus, a resummation is possible where we use the Neumann expansion $1 = J_0 + 2J_2 + 2J_4 + \cdots$. Specifically, we have

$$F(t) = e^{-\alpha^2 t^2}\left[\left(J_0 + \sum_{n=1}^{\infty} 2J_{2n}\right) + \sum_{n=1}^{\infty} \Delta a_{2n} J_{2n}\right],$$

$$= e^{-\alpha^2 t^2}\left(1 + \sum_{n=1}^{\infty} \Delta a_{2n} J_{2n}(\beta t)\right).$$

This result is expected since if $F(t) = 1$, the series of Bessel functions represents $\exp(\alpha^2 t^2)$. Other expansions given by (10) can therefore be resummed to give a leading term of either $\exp(-\alpha t)$ or $\exp(-\alpha^2 t^2)$, so that an FID curve which is very nearly exponential or Gaussian could be represented by these modified series where terms other than the first would describe small corrections to the presummed behavior. This result suggests that further resummations are possible. Using (7) we have, for example,

$$a_2 = 2 + \delta a_2, \quad a_4 = 2 + 4\delta a_2 + \delta a_4,$$

$$a_6 = 2 + 9\delta a_2 + 6\delta a_4 + \delta a_6,$$

where δa_{2n} is proportional to $f^{(2n)}(0)$. Collecting coefficients of δa_{2n} in (13) we obtain

$$\begin{aligned} F(t) = e^{-\alpha^2 t^2}[&(J_0 + 2J_2 + 2J_4 + \cdots) \\ &+ \delta a_2(J_2 + 4J_4 + 9J_6 + \cdots) \\ &+ \delta a_4(J_4 + J_6 + \cdots) + \cdots]. \end{aligned} \tag{14}$$

But consider the following Neumann expansions:

$$(1/2!)(\tfrac{1}{2}t)^2 = J_2 + 4J_4 + 9J_6 + \cdots,$$

$$(1/4!)(\tfrac{1}{2}t)^4 = J_4 + 6J_6 + \cdots.$$

These expansions suggest that (14) may be written as

$$F(t) = e^{-\alpha^2 t^2}\sum_{n=0}^{\infty} C_{2n}\, t^{2n}/(2n)!. \tag{15}$$

This may be proved by using (7) and (13). Collecting coefficients of $f^{(k)}(0)$ in the expansions we may write

$$\begin{aligned} e^{\alpha^2 t^2}F(t) = J_0 &+ \sum_{n=1}^{\infty} 2J_{2n}\left(\frac{f^{(0)}(0)}{\beta^0}\right) \\ &+ \sum_{n=1}^{\infty} 2J_{2n}\left[\frac{2^4 n}{n+2}\binom{n+1}{2}\frac{f^{(2)}(0)}{\beta^2}\right] \\ &+ \sum_{n=1}^{\infty} 2J_{2n}\left[\frac{2^4 n}{n+2}\binom{n+2}{4} \times\frac{f^{(4)}(0)}{\beta^4}\right] + \cdots. \end{aligned} \tag{16}$$

The Neumann expansion for $(\frac{1}{2}t)^n$ is[17]

$$(\tfrac{1}{2}t)^n = \sum_{m=0}^{\infty} \frac{(n+2m)\Gamma(n+m)}{m!} J_{n+2m}(t).$$

When this is used to evaluate the sums in (16) we obtain, in accordance with (15),

$$\begin{aligned} e^{\alpha^2 t^2}F(t) = 1 &+ (\beta^2 t^2/2!)[f^{(2)}(0)/\beta^2] \\ &+ (\beta^4 t^4/4!)[f^{(4)}(0)/\beta^4] + \cdots, \end{aligned}$$

which is just a Taylor series for the even function $f(t) = e^{\alpha^2 t^2}F(t)$ which could have been written down immediately. For lines which are nearly Gaussian it would, therefore, be natural to use the expansion theorem

$$F(t) = e^{-\alpha^2 t^2}\sum_{n=0}^{\infty} f^{(2n)}(0)\frac{t^{2n}}{(2n)!}. \tag{17}$$

If $\alpha = 0$, we recover (1). Another way of obtaining (17) would be to take the Fourier transform of the Gram-Charlier series for $G(\omega)$.[18] This expansion represents $G(\omega)$ as a Gaussian function times an infinite series of Hermite polynomials. The Fourier transform of this expansion gives (17).

Another use of theorems (8) or (10) is the evaluation of moments from a given FID curve. Successive coefficients may be evaluated using the orthogonality integral for Bessel functions,[19]

$$\int_0^{\infty}\frac{dt}{t} J_{\nu+2n+1}(t) J_{\nu+2m+1}(t) = \frac{\delta_{nm}}{2(2n+\nu+1)},$$

which is valid, provided $2n + \nu + 1 > 0$. As an illustration consider the expansion (10) for $\nu = \frac{1}{2}$,

$$e^{\alpha^2 t^2}F(t) = \sum_{n=0}^{\infty}\frac{b_{2n} J_{2n+1/2}(\beta t)}{(\beta t)^{1/2}} = \sum_{n=0}^{\infty} a_{2n} j_{2n}(\beta t),$$

where $j_{2n}(z)$ is spherical Bessel function and $b_{2n} = (\frac{1}{2}\pi)^{1/2} a_{2n}$. Using the orthogonality integral, we obtain

$$a_{2n} = (4/\pi)(2n + \tfrac{1}{2})\int_0^{\infty} e^{\alpha^2 t^2}F(t)\, j_{2n}(\beta t)\, d(\beta t).$$

Choosing $\alpha = 0$, $n = 1$, and using (9) and (12), we have

$$\left(1 - \frac{3M_2}{\beta^2}\right) = \left(\frac{4}{\pi}\right)\int_0^{\infty} F(t)\, j_2(\beta t)\, d(\beta t),$$

where β may be chosen for convenience in evaluating the integral. Of course, α may be chosen to be nonzero, although it might not be practical to do so. Higher moments may be evaluated in the same manner.

In summary, the expansion theorem (10) and its various forms such as (8) and (17) provide exact uniformly convergent expansions for the FID functions.

III. APPLICATION TO CALCIUM FLUORIDE

We have applied the expansion theorem (10) to the F^{19} resonance in calcium fluoride (CaF_2) for [100] and [111] orientations of external field. Since Abragam's trial function (3) is an excellent approximation and corresponds to choosing $\nu=\frac{1}{2}$, we have considered in addition $\nu=0$ and $\nu=1$.

Consider first the case where $\nu=\frac{1}{2}$. We will show how Abragam's results may be obtained. Using (10) and defining $a_{2n}=(2/\pi)^{1/2}b_{2n}$, we have

$$F(t)=e^{-\alpha^2t^2}\sum_{n=0}^{\infty}a_{2n}j_{2n}(\beta t), \tag{18}$$

where j_{2n} is the spherical Bessel function of order $2n$. The first few coefficients obtained using (9) and (12) are

$$a_0=1, \quad a_2=\tfrac{5}{2}[1+3(2\alpha^2-M_2)/\beta^2],$$

$$a_4=\tfrac{27}{8}[1+10(2\alpha^2-M_2)/\beta^2 + 35(M_4-12\alpha^2M_2+12\alpha^4)/3\beta^4].$$

Choosing α and β so as to make $a_2=a_4=0$, we obtain

$$\begin{aligned}\beta^2&=M_2[\tfrac{15}{2}(3-M_4/M_2^2)]^{1/2},\\ \alpha^2&=\tfrac{1}{2}M_2\{1-[\tfrac{5}{6}(3-M_4/M_2^2)]^{1/2}\}.\end{aligned} \tag{19}$$

These values of α and β are identical to those used by Abragam[12] in applying (3), that is, they ensure that (3) gives the correct second and fourth moments when expanded as in (1). Requiring α and β to be real numbers means that the following inequalities must be satisfied:

$$(3-M_4/M_2^2)\geqq 0, \quad [\tfrac{5}{6}(3-M_4/M_2^2)]^{1/2}\leqq 1 .$$

These inequalities are satisfied for calcium fluoride; for example, $M_4/M_2^2=2.03$ for [100] orientation of external field.[20] For a Gaussian line $M_4/M_2^2=3$ and $\beta=0$ as required.

For $\nu=0$ we have

$$F(t)=e^{-\alpha^2t^2}\sum_{n=0}^{\infty}a_{2n}J_{2n}(\beta t), \tag{20}$$

where the first three coefficients are

$$a_0=1, \quad a_2=2+4(2\alpha^2-M_2)/\beta^2 ,$$

$$a_4=2+16(2\alpha^2-M_2)/\beta^2 + 16(M_4-12\alpha^2M_2+12\alpha^4)/\beta^4.$$

We require $a_2=a_4=0$ to obtain

$$\begin{aligned}\beta^2&=M_2[\tfrac{8}{3}(3-M_4/M_2^2)]^{1/2},\\ \alpha^2&=\tfrac{1}{2}M_2\{1-[\tfrac{4}{6}(3-M_4/M_2^2)]^{1/2}\}.\end{aligned} \tag{21}$$

This choice of α and β means that

$$e^{-\alpha^2t^2}J_0(\beta t)=1-M_2(t^2/2!)+M_4(t^4/4!)+\cdots .$$

For calcium fluoride both α and β will be real numbers.

For $\nu=1$ we obtain

$$F(t)=e^{-\alpha^2t^2}\sum_{n=0}^{\infty}a_{2n}J_{n+1}(\beta t)/\beta t . \tag{22}$$

The coefficients through $n=2$ are

$$a_0=2,$$

$$a_2=6[1+4(2\alpha^2-M_2)/\beta^2],$$

$$a_4=10[1+12(2\alpha^2-M_2)/\beta^2 + 16(M_4-12\alpha^2M_2+12\alpha^4)/\beta^2].$$

The condition $a_2=a_4=0$ gives

$$\begin{aligned}\beta^2&=M_2[16(3-M_4/M_2^2)]^{1/2} ,\\ \alpha^2&=\tfrac{1}{2}M_2[1-(3-M_4/M_2^2)^{1/2}] .\end{aligned} \tag{23}$$

Again, α and β for calcium fluroide are real numbers and using (23),

$$e^{-\alpha^2t^2}\frac{J_1(\beta t)}{\beta t}=1-M_2\frac{t^2}{2!}+M_4\frac{t^4}{4!}+\cdots .$$

Expansions for $\nu=+\frac{3}{2}$ and $\nu=-\frac{1}{2}$ were also examined. For $\nu=\frac{3}{2}$ we obtain, as before,

$$\alpha^2=\tfrac{1}{2}M_2\{1-[\tfrac{7}{6}(3-M_4/M_2^2)]^{1/2}\} .$$

Notice, however, that α^2 will be negative when $M_4/M_2^2=2.03$. This choice of α and β will cause the leading term to be a satisfactory approximation only for very short times, and it is therefore not considered further. For $\nu=-\frac{1}{2}$, we obtain

$$F(t)=e^{-\alpha^2t^2}\left(\cos\beta t+\sum_{n=1}^{\infty}a_{2n}(\beta t)j_{2n-1}(\beta t)\right),$$

where the condition $a_2=a_4=0$ gives

$$\beta^2=M_2[\tfrac{1}{2}(3-M_4/M_2^2)]^{1/2},$$

$$\alpha^2=\tfrac{1}{2}M_2\{1-[\tfrac{1}{2}(3-M_4/M_2^2)]^{1/2}\}.$$

Using these values of α and β, we find that this leading term is in poorer agreement with experiment than the corresponding terms for $\nu=0$ or $\nu=1$.

We have calculated the FID shape in CaF_2 for [100] orientation using the leading terms of (18), (20), and (22) with α and β being determined by (19), (21), and (23), respectively. Comparison with data of Barnaal and Lowe[21] is made in Fig. 1. The agreement is excellent for $\nu=\frac{1}{2}$ for the whole range of the observed decay. The results for $\nu=0$ and $\nu=1$ tend to bracket the $\nu=\frac{1}{2}$ curve. For the [111] orientation we have found the difference between curves for $\nu=\frac{1}{2}$ and $\nu=1$ to be less than for the [100] orientation, and agreement with the data is similar to that shown in Fig. 1 for $\nu=\frac{1}{2}$. The problem of determining the optimum leading term

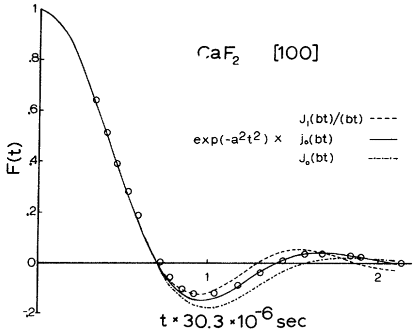

FIG. 1. Experimental FID shape from calcium fluoride for [100] orientation of external field compared with the leading terms of three different Neumann expansions. The experimental data of Barnaal and Lowe are plotted as circles, and the functional form of the theoretical curves is indicated.

in (10) has thus been solved for CaF$_2$. The final question we consider for expansions (18), (20), and (22) is how many terms are necessary for them to give the same FID curve for CaF$_2$. This requires a knowledge of some of the higher moments of the line which is less than complete. Abragam[12] has determined M_6 and M_8 using some of Bruce's data.[3] The theoretical M_6 has been calculated approximately to be $M_6/M_2^3 = 4.88$ for the [100] orientation[22]; however, the experimental value determined by Abragam is $M_6/M_2^3 = 5.49$. Using the values of M_6 and M_8 tabulated by Abragam we have calculated FID curves using (18), (20), and (22), with terms through a_8 being included; theoretical values were used for M_2 and M_4.[20] We find that all three truncated expansions give essentially the same FID curve for the first 75% of the decay. Furthermore, these curves are quite sensitive to the values M_6 and M_8 since the last two terms of these truncated expansions involve the difference between terms of about the same magnitude but opposite sign. For example, changing M_6 and M_8 as given by Abragam, by amounts equivalent to corrections[23] for modulation distortion, produces differences as large as 10%, even though the moment ratios have changed by only 1 or 2%. Since the uncertainties in the values of M_6 and M_8 are larger than this, we have not compared, in detail, experimental and calculated curves for these truncated expansions. However, when we correct M_6 and M_8 for the modulation used by Bruce[3] we obtain a FID curve which is nearly equal to the result for $\nu = \frac{1}{2}$ plotted in Fig. 1 for the first 75% of the decay.

IV. SUMMARY

We have found an exact expression or expansion theorem for a FID curve which involves all the moments of the corresponding cw absorption line as well as two scale factors or parameters which may be chosen to optimize the convergence which is necessarily uniform. The expression obtained is a generalization of Taylor's theorem known as a Neumann expansion. Application of this expansion theorem to FID curves from calcium fluoride shows that it is possible to obtain an excellent fit to the data using only the theoretical second and fourth moments for the expansion whose leading term corresponds to Abragam's trial function. Furthermore, when several exact but different expansions were truncated to only three terms it was found that they were nearly equal to each other and to the data over a major portion of the decay for the optimum choice of the two parameters involved.

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Antiresonance in the Optical Spectra of Transition-Metal Ions in Crystals*

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When a sharp absorption line of a defect or impurity center is overlapped by a broad vibronic band, interference can occur between the two types of transition. We find several examples of this effect in the optical spectrum of V^{2+} in octahedral fluoride coordination. The spectral line shapes can be fitted well by the four-parameter theory of Fano, which was developed to account for the interference of a sharp intra-atomic transition with an overlapping ionizing continuum. We justify the application of this theory to the vibronic problem, and calculate some of the parameters in terms of other spectroscopic data, obtaining good agreement with experiment.

I. INTRODUCTION

Among the more remarkable features of the spectra of the rare gases are the Beutler bands.[1,2] These occur when sharp intra-atomic transitions are overlapped by a broad ionizing continuum. The transition matrix elements interfere destructively on one side of the intra-atomic resonance and constructively on the other, giving a characteristic "antiresonant" spectral line shape. A particularly elegant example is to be seen in the hard ultraviolet absorption spectrum of He I[3]; the $1s^2 \rightarrow 2s$, np series looks like a series of dispersion curves superimposed on the continuum of ionizing transitions which leave the He^+ ion in the $1s$ state. Similar effects are to be expected in the predissociation region of molecular spectra.[4]

The theory of this effect has been given by Fano.[5] The formalism is identical to that of the Breit-Wigner[6] theory of scattering from resonant nuclei. Fano shows that if the continuum absorption $\alpha_B(\omega)$ is slowly varying in the vicinity of an isolated resonance, the absorption coefficient $\alpha(\omega)$ is given by

$$\alpha(\omega)=\alpha_B(\omega)+\alpha_0(q^2+2\xi q-1)/(1+\xi^2)\ , \qquad (1)$$

where

$$\xi=(\omega-\omega_r)/\gamma\ , \qquad q=\frac{\langle s'|\vec{P}|a\rangle}{\pi\langle s|\mathcal{H}_i|c\rangle\langle c|\vec{P}|a\rangle}\ ,$$

$$\frac{\alpha_0}{\alpha_B}=\frac{|\langle c|\vec{P}|a\rangle|^2}{|\langle b|\vec{P}|a\rangle|^2}\equiv p\ , \qquad \gamma=\pi|\langle c|\mathcal{H}_i|s\rangle|^2\ .$$

Here $|s\rangle$ is the sharp excited state; $|s'\rangle$ is that state modified by the interaction Hamiltonian $\mathcal{H}_i$, which connects $|s\rangle$ to a certain fraction $|c\rangle$ of the continuum states $|b\rangle$. The energy of $|s'\rangle$ above the ground state $|a\rangle$ is $\hbar\omega_r$, and γ^{-1} can be interpreted as the lifetime of the sharp state against decay to the continuum. $\vec{P}$ is the electric- or magnetic-dipole operator. The quantity q may take any value between $-\infty$ and $+\infty$, and $q^2\gamma$ is a measure of the strength of transitions to the modified sharp state $|s'\rangle$, relative to the continuum $|c\rangle$.

Equation (1) can be represented by a family of curves corresponding to different values of q, as shown, normalized by a factor $(1+q^2)^{-1}$, in Fig. 1.