Sixth and Eighth Moments of the Magnetic-Resonance Lines of a Dipolar-Coupled Rigid Lattice

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(Received 3 October 1972)

Analytical expressions for the sixth and eighth moments of the magnetic-resonance lines of a dipolar-coupled rigid lattice are obtained by performing the commutations of angular momentum operators and the necessary reductions by means of a computer. The expressions are used to derive numerical values of the moments for a simple cubic lattice for varying numbers of interacting neighbors. The sixth and eighth moments predicted from Abragam's trial function for the free-induction-decay curve are compared to the corresponding exact moments reported here. We also present a straightforward method for the algebraic computer calculation of traces of angular momentum operators.

I. INTRODUCTION

In 1948 Van Vleck[1] studied the dipolar broadening of the magnetic-resonance lines in crystals by the method of moments. He gave general expressions for the second and fourth moments.

The higher moments, which are difficult to calculate due to the larger number of noncommuting spin operators, are important in determining the character of the line shape[2] and in investigations of the accuracy of experimentally determined line shapes.[3] The moments also play a dominant role in the error-bound theory[4] of magnetic-resonance line shapes. This theory allows calculation of the error bounds of the line shape from the known moments, and the usefulness of this approach is therefore increased as higher moments become known. Furthermore, knowledge of the moments are of importance in various recent expansion theories[5,6] for the line shape. Parker[5] has recently described an expansion of the free-induction-decay curve in spherical Bessel functions. The nth expansion coefficient is a function of the first n moments of the line shape. Parker[5] has rearranged the expansion to yield Abragam's trial function for the free-induction-decay curve as the first term. In this form of the expansion knowledge of the second and fourth moments suffices to determine the first term only. Thus an evaluation of the usefulness of the expansion in describing the free-induction-decay curve in the time region where Abragam's trial function is inadequate, requires a knowledge of the moments of order higher than four.

In this paper we present analytical expressions for the sixth and eighth moments. The expressions were obtained by letting a computer perform the necessary algebraic operations.

In Sec. II we describe the procedure employed, and in Sec. III we give the expressions for the moments. Numerical values are given for the sixth and eighth moments for a simple cubic lattice in Sec. IV, and in Sec. V we derive the sixth and eighth moments from Abragam's trial function and compare them to our exact values. Finally, in Sec. VI we discuss our expression for the sixth moment in relation to some recently published results.[7,8]

II. THEORY AND METHOD

We consider a system of N identical spins $\vec{I}^j = (I_x^j, I_y^j, I_z^j)$ in a rigid lattice subject to an external magnetic field $\vec{B}_0$. The spins are coupled by a dipolar Hamiltonian, and we assume that $|\vec{B}_0|$ is so large that only the terms of the truncated dipolar Hamiltonian influence the line shape significantly.[1] The truncated dipolar interaction is

$$H = \frac{\gamma^2\hbar^2}{4}\sum_j^N\sum_k^N (3I_z^jI_z^k - \vec{I}^j\cdot\vec{I}^k)\frac{1-3\cos^2\theta_{jk}}{r_{jk}^3}$$
$$\equiv \gamma^2\hbar^2\sum_j^N\sum_k^N B_{jk}\sum_{q=x,y,z} C_q I_q^j I_q^k, \tag{1}$$

where θ_{jk} is the angle between $\vec{B}_0$ and the vector $\vec{r}_{jk}$ connecting the jth and kth spin. γ is the magnetogyric ratio of the nucleus, $C_x = C_y = -\frac{1}{2}C_z = -\frac{1}{6}$, and

$$B_{jk} = \tfrac{3}{2}(1-3\cos^2\theta_{jk})/r_{jk}^3 \quad (j\neq k),$$
$$B_{jj} = 0. \tag{2}$$

The magnetic resonance spectrum $G(\omega)$, where ω is measured relative to the center of the line, is given in the high-temperature approximation by[2]

$$G(\omega) = (1/2\pi)\int_{-\infty}^{\infty} F(t)e^{i\omega t}dt, \tag{3}$$

where $F(t)$ is the autocorrelation function for M_x, the x component of the magnetization;

$$F(t) = \mathrm{Tr}(M_x e^{iH^{\times}t/\hbar}M_x)/\mathrm{Tr}M_x^2, \tag{4}$$

$$M_x = \gamma\hbar\sum_j^N I_x^j. \tag{5}$$

$H^{\times}$ is the superoperator corresponding to the truncated dipolar Hamiltonian in Eq. (1),

$$H^{\times}\ldots=[H,\ldots]. \tag{6}$$

$G(\omega)$ is an even function of ω. The even moments of $G(\omega)$ are

$$M_{2n}=\int_{-\infty}^{\infty}\omega^{2n}G(\omega)d\omega=(-1)^n\frac{d^{2n}F(t)}{dt^{2n}}\bigg|_{t=0}, \tag{7}$$

since $\int_{-\infty}^{\infty}G(\omega)d\omega$ is unity. The $2n$th time derivative of Eq. (4) evaluated at $t=0$ is

$$\frac{d^{2n}F(t)}{dt^{2n}}\bigg|_{t=0}=(-\hbar^{-2})^n\,\mathrm{Tr}(M_x(H^{\times})^{2n}M_x)/\mathrm{Tr}\,M_x^2. \tag{8}$$

Since

$$\mathrm{Tr}(M_xH^{\times}\boldsymbol{A})=-\mathrm{Tr}((H^{\times}M_x)\boldsymbol{A}), \tag{9}$$

where $\boldsymbol{A}$ is an arbitrary operator, we get

$$M_{2n}=(-\hbar^{-2})^n\,\mathrm{Tr}([(H^{\times})^nM_x]^2)/\mathrm{Tr}\,M_x^2. \tag{10}$$

It is difficult to evaluate Eq. (10) for $n>2$ manually due to the large number of terms arising from noncommuting spin operators. We have therefore utilized a computer to perform the commutations, the squaring of the commutator and the necessary reductions.

The computer is "taught" the simple commutation rules for angular momentum operators:

$$[I_{q_1}^{j},I_{q_2}^{k}]=\beta_{q_1q_2q_3}I_{q_3}^{j}\,\delta_{jk}, \tag{11}$$

where

$$\beta_{q_1q_2q_3}=\begin{cases} i & \text{for } (q_1q_2q_3)=(xyz),(yzx),(zxy)\\ -i & \text{for } (q_1q_2q_3)=(xzy),(yxz),(zyx)\\ 0 & \text{otherwise.}\end{cases}$$

The general term in $(H^{\times})^nI_x$ is

$$\gamma^{2n}\hbar^{2n}\sum_{j,k}\sum_{j_1,\ldots,j_n}[C_qB_{jk}I_q^jI_q^k,\ \times D\,E(j_1,\ldots,j_n)I_{q_1}^{j_1}\cdots I_{q_n}^{j_n}]. \tag{12}$$

Here $E(j_1,\ldots,j_n)$ is a product of B_{rs} [Eq. (2)], where r and s belong to the set of summation variables $\{j_1,\ldots,j_n\}$ and D is a product of C_q and $\beta_{q_1q_2q_3}$ accumulated through the first $n-1$ commutations. We express Eq. (12) as

$$\gamma^{2n}\hbar^{2n}C_qDB_{jk}E(j_1,\ldots,j_n)\Bigg[\sum_{p=1}^{n}I_q^j\Bigg(\prod_{m=1}^{p-1}I_{q_m}^{j_m}\Bigg)\times[I_q^k,I_{q_p}^{j_p}]\Bigg(\prod_{m=p+1}^{n}I_{q_m}^{j_m}\Bigg)+\sum_{p=1}^{n}\Bigg(\prod_{m=1}^{p-1}I_{q_m}^{j_m}\Bigg)[I_q^j,I_{q_p}^{j_p}]\Bigg(\prod_{m=p+1}^{n}I_{q_m}^{j_m}\Bigg)I_q^k\Bigg] \tag{13}$$

and use the commutation rules in Eq. (11) to reduce Eq. (13).

The number of terms appearing in $(H^{\times})^nI_x$ may be reduced by commuting $I_{q_1}^{j_1}I_{q_m}^{j_m}$ in the terms which contain the factor $B_{j_1j_m}$ and comparing terms.

The final expression for $(H^{\times})^nI_x$ is squared and M_{2n} becomes a sum of traces having the form

$$\mathrm{Tr}\Bigg(\sum_{j_1,\ldots,j_h}E(j_1,\ldots,j_h)I_{q_1}^{j_1}\cdots I_{q_h}^{j_h}\Bigg)=\sum_{j_1,\ldots,j_h}E(j_1,\ldots,j_h)\,\mathrm{Tr}\,(I_{q_1}^{j_1}\cdots I_{q_h}^{j_h}), \tag{14}$$

where $h=2n+2$.

The sum in Eq. (14) is an unrestricted sum, i.e., all summation variables take on all possible values independently. This unrestricted sum may be transformed into a sum of restricted sums, restricted in the sense that no pair of summation variables may take on the same value simultaneously. This transformation is given by

$$\sum_{j_1,\ldots,j_h}P(j_1,\ldots,j_h)=\sum_{G}\sum_{k_1,\ldots,k_{u_G}}{}'\,P^G(k_1,\ldots,k_{u_G}), \tag{15}$$

where $P(j_1,\ldots,j_h)=E(j_1,\ldots,j_h)I_{q_1}^{j_1}\cdots I_{q_h}^{j_h}$. A prime on the summation sign indicates a restricted sum. In the Gth restricted sum the variables $j_1,\ldots,j_h$ are divided in u_G groups, and all variables in a group are substituted by a single new variable. $P^G(k_1,\ldots,k_{u_G})$ is obtained by making this substitution in $P(j_1,\ldots,j_h)$. Thus the sum $\sum_G$ is a sum over all such groupings of the summation variables $j_1,\ldots,j_h$.

Using the transformation [Eq. (15)], in Eq. (14) gives

$$\begin{aligned}\sum_{j_1,\ldots,j_h}E(j_1,\ldots,j_h)\,\mathrm{Tr}(I_{q_1}^{j_1}\cdots I_{q_h}^{j_h})&=\sum_{G}\sum_{k_1,\ldots,k_{u_G}}{}'E^G(k_1,\ldots,k_{u_G})\,\mathrm{Tr}\Bigg(\prod_{p=1}^{u_G}O_p^{G,k_p}\Bigg)\\&=\sum_{G}(2I+1)^{N-u_G}\Bigg(\prod_{p=1}^{u_G}\mathrm{Tr}\,(O_p^G)\Bigg)\times\Bigg(\sum_{k_1,\ldots,k_{u_G}}{}'E^G(k_1,\ldots,k_{u_G})\Bigg).\end{aligned} \tag{16}$$

All the spin operators belonging to the summation variable k_p are collected in the operator O_p^{G,k_p}. The trace $\mathrm{Tr}O_p^G$ is a one-spin trace of the one-spin operator O_p^G. In Eq. (16) we omit all restricted sums where $E^G(k_1,\ldots,k_{u_G})$ contains a factor of $B_{k_ik_i}$.

To illustrate this procedure we perform the expansion Eq. (16) on a term from the fourth moment:

$$\mathrm{Tr}\Bigg(\sum_{j_1,\ldots,j_6}B_{j_1j_3}B_{j_2j_3}B_{j_4j_6}B_{j_5j_6}I_z^{j_1}I_z^{j_2}I_x^{j_3}I_y^{j_4}I_y^{j_5}I_x^{j_6}\Bigg)=(2I+1)^{N-3}\,\mathrm{Tr}(I_x^2)\,\mathrm{Tr}(I_y^2)\,\mathrm{Tr}(I_z^2)\sum_{k_1k_2k_3}{}'B_{k_1k_2}^2B_{k_2k_3}^2$$

$$+(2I+1)^{N-2}\,\mathrm{Tr}(I_z^2 I_y^2)\,\mathrm{Tr}(I_x^2)\sum_{k_1k_2}{}' B_{k_1k_2}^4. \quad (17)$$

In the first sum we have collected the terms with $j_1=j_2=k_1, j_3=j_6=k_2$, and $j_4=j_5=k_3$ and in the second sum we have set $j_1=j_2=j_4=j_5=k_1$ and $j_3=j_6=k_2$. All other combinations of the indices yield traces equal to zero.

The splitting of a product of spin operators into different groups is greatly simplified by using the fact that $\mathrm{Tr}O_p$ vanishes unless O_p contains all the operators I_x, I_y, and I_z in even numbers, or all three operators in uneven numbers.[9]

All the necessary traces for the evaluation of the moments up to M_8 may be found in Ref. 9 or they may easily be evaluated algebraically on a computer as described in the Appendix. The traces are polynomials in $X\equiv I(I+1)$.

We can therefore express the moments as

$$M_{2n}=(\gamma^2\hbar)^{2n}\sum_{j=1}^{n} W_j^{2n}\,X^j \quad (18)$$

by multiplying the traces according to Eq. (16). W_j^{2n} is a combination of the restricted sums in Eq. (16). These sums are reduced to sums which involves summations over the smallest possible number of indices by using relations such as

$$N^{-1}\sum_{k_1k_2k_3}{}' B_{k_1k_2}^2 B_{k_2k_3}^2=\left(N^{-1}\sum_{k_1k_2}{}' B_{k_1k_2}^2\right)^2-N^{-1}\sum_{k_1k_2}{}' B_{k_1k_2}^4, \quad (19)$$

where all summation indices are different.

When we use relations as Eq. (19) we can no longer identify the lattice terms as terms arising from interaction of 2, 3, . . . , $n+1$ spins in the sense of Bersohn and Das.[10] However, the total number of terms is substantially reduced and the numerical calculation is simplified.

It should be pointed out that the time requirement rises sharply when going to higher moments, for example, the calculation of M_8 uses approximately 1200 times as much computing time as M_6. The major part of the computation time is used in performing the expansion in Eq. (16).

III. ANALYTICAL RESULTS

The obtained analytical expressions for M_8 and M_6 are given in terms of the following quantities:

$$S_m=N^{-1}\sum_{j,k}{}' B_{jk}^m, \quad (20)$$

$$R_{jk}(pq)=\sum_{l}{}' B_{jl}^p B_{lk}^q \quad (j\neq k), \quad (21)$$

and

$$Q(pqr)=N^{-1}\sum_{j,k,l,m}{}' B_{jk}^p B_{jl}^q B_{jm}B_{kl}B_{km}B_{lm}^r; \quad (22)$$

$$\begin{aligned}
M_8=\frac{\gamma^{16}\hbar^8}{32\,805}\Big\{X^4\Big[&18\,385S_2^4+\frac{5\,101\,107}{896}S_4^2-\frac{47\,648}{7}S_8-32\,520S_4S_2^2+222S_3^2S_2+\frac{20\,015\,923}{896}S_6S_2-\frac{2\,240\,717}{448}S_5S_3\\
&+\frac{772\,447}{256}B_{jk}^6R_{jk}(11)-\frac{147\,573}{64}B_{jk}^5R_{jk}(21)+\frac{2\,804\,121}{1792}B_{jk}^4R_{jk}(31)+\frac{43\,779\,481}{1792}B_{jk}^4R_{jk}(22)\\
&-\frac{292\,981}{128}B_{jk}^3R_{jk}(32)+1360B_{jk}R_{jk}(41)R_{jk}(11)+2240B_{jk}R_{jk}(32)R_{jk}(11)+3344B_{jk}R_{jk}(31)R_{jk}(21)\\
&+632B_{jk}R_{jk}(22)R_{jk}(21)-1720B_{jk}R_{jk}(21)R_{jk}^2(11)+1640B_{jk}^2R_{jk}^3(11)-30\,480B_{jk}^2R_{jk}(31)R_{jk}(11)\\
&-3648B_{jk}^2R_{jk}(22)R_{jk}(11)+6500B_{jk}^2R_{jk}^2(21)-1140\Big(\sum_k{}' B_{jk}^2R_{jk}(11)\Big)^2+4928B_{jk}^3R_{jk}(21)R_{jk}(11)\\
&-6780B_{jk}^4R_{jk}^2(11)+3690R_{jk}(22)R_{jk}^2(11)+2512R_{jk}(42)R_{jk}(11)-1720R_{jk}^2(21)R_{jk}(11)\\
&-2744R_{jk}^2(31)+1640R_{jk}(31)R_{jk}(22)-2498R_{jk}^2(22)+6370S_2^2B_{jk}^2R_{jk}(11)-8220S_2B_{jk}^4R_{jk}(11)\\
&-1792S_2B_{jk}^3R_{jk}(21)-20\,550S_2B_{jk}^2R_{jk}(22)+1076S_3B_{jk}^3R_{jk}(11)-664S_3B_{jk}^2R_{jk}(21)\\
&-1822S_4B_{jk}^2R_{jk}(11)+24\,300S_2B_{jk}^2R_{jk}^2(11)-3320S_2B_{jk}R_{jk}(21)R_{jk}(11)-2870S_2R_{jk}^2(21)\\
&-920B_{jk}^2B_{jl}B_{kl}R_{jk}(11)R_{jl}(11)+12\,960B_{jk}^2B_{jl}B_{kl}R_{jl}(11)R_{kl}(11)-4480B_{jk}B_{jl}B_{kl}R_{jk}(21)R_{jl}(11)\\
&-1820B_{jk}^2B_{kl}^2R_{jk}(11)R_{jl}(11)+180B_{jk}^2B_{jl}R_{kl}(21)R_{jl}(11)-2000B_{jk}B_{kl}R_{jk}(21)R_{jl}(21)\\
&-50B_{jk}^2R_{jl}(22)R_{kl}(11)-240B_{jk}B_{jl}\Big(\sum_m{}' B_{jm}B_{km}B_{lm}\Big)^2+944Q(221)+4224Q(311)-8468Q(212)-2000S_2Q(111)\\
&-420B_{jk}R_{jk}(11)B_{jl}B_{jm}B_{kl}B_{km}B_{lm}-720B_{jk}R_{jl}(21)B_{jm}B_{kl}B_{km}B_{lm}\\
&-1000B_{jk}^2B_{jl}B_{jm}B_{kl}R_{km}(11)B_{lm}-580B_{jk}B_{jl}B_{jm}^2R_{kl}(11)B_{km}B_{lm}\Big]
\end{aligned}$$

$$+\frac{X^3}{2}\left(\frac{5\,866\,291}{448}S_4^2-\frac{13\,063\,987}{896}S_8-39\,390S_4S_2^2+6972S_3^2S_2+\frac{17\,172\,019}{448}S_6S_2-\frac{10\,521\,907}{896}S_5S_3\right.$$
$$+\frac{358\,809}{896}B_{jk}^6R_{jk}(11)-\frac{2\,012\,851}{224}B_{jk}^5R_{jk}(21)-\frac{2\,990\,131}{448}B_{jk}^4R_{jk}(31)+\frac{47\,674\,521}{896}B_{jk}^4R_{jk}(22)$$
$$-\frac{5\,875\,507}{448}B_{jk}^3R_{jk}(32)+3360B_{jk}R_{jk}(41)R_{jk}(11)+8940B_{jk}R_{jk}(32)R_{jk}(11)+4044B_{jk}R_{jk}(31)R_{jk}(21)$$
$$+1782B_{jk}R_{jk}(22)R_{jk}(21)-44\,760B_{jk}^2R_{jk}(31)R_{jk}(11)+192B_{jk}^2R_{jk}(22)R_{jk}(11)+8160B_{jk}^2R_{jk}^2(21)$$
$$+10\,728B_{jk}^3R_{jk}(21)R_{jk}(11)-7845B_{jk}^4R_{jk}^2(11)+3732R_{jk}(42)R_{jk}(11)-6324R_{jk}^2(31)$$
$$+3210R_{jk}(31)R_{jk}(22)-1818R_{jk}^2(22)+3630S_2B_{jk}^4R_{jk}(11)+9528S_2B_{jk}^3R_{jk}(21)-23\,715S_2B_{jk}^2R_{jk}(22)$$
$$\left.+1416S_3B_{jk}^3R_{jk}(11)+2946S_3B_{jk}^2R_{jk}(21)-1182S_4B_{jk}^2R_{jk}(11)+2724Q(221)+4704Q(311)-11\,073Q(212)\right)$$
$$+\frac{X^2}{1792}[4\,906\,137S_4^2-5\,706\,547S_8+9\,260\,697S_6S_2-3\,880\,396S_5S_3-1\,657\,497B_{jk}^6R_{jk}(11)-3\,612\,211B_{jk}^5R_{jk}(21)$$
$$-5\,680\,281B_{jk}^4R_{jk}(31)+16\,790\,630B_{jk}^4R_{jk}(22)-5\,289\,753B_{jk}^3R_{jk}(32)]-X\frac{297\,043}{448}S_8\Big\}, \quad (23)$$

$$M_6=\frac{\gamma^{12}\hbar^6}{135}\left[\frac{X^3}{27}\left(\frac{12\,844}{35}S_6+40S_3^2+1145S_2^3-1220S_4S_2-232B_{jk}^4R_{jk}(11)-192B_{jk}^3R_{jk}(21)-370B_{jk}^2R_{jk}(22)\right.\right.$$
$$\left.+520S_2B_{jk}^2R_{jk}(11)+420B_{jk}^2R_{jk}^2(11)+20B_{jk}R_{jk}(21)R_{jk}(11)-40R_{jk}^2(21)-40Q(111)\right)$$
$$\left.+\frac{X^2}{6}\left(\frac{1982}{35}S_6+10S_3^2-115S_4S_2-3B_{jk}^4R_{jk}(11)+2B_{jk}^3R_{jk}(21)-40B_{jk}^2R_{jk}(22)\right)+X\frac{68}{35}S_6\right]. \quad (24)$$

The summation signs have been dropped except in the cases where it is not obvious which indices we are summing over. All indices must be different and one of the indices is supposed to be fixed. For the sake of completeness we also list M_4 and M_2, which were first given by Van Vleck[1]:

$$M_4=\tfrac{1}{30}\gamma^8\hbar^4\{X^2[\tfrac{70}{9}S_2^2-\tfrac{28}{9}S_4+\tfrac{20}{9}B_{jk}^2R_{jk}(11)]-XS_4\}, \quad (25)$$

$$M_2=\tfrac{1}{3}\gamma^4\hbar^2S_2X. \quad (26)$$

IV. NUMERICAL RESULTS

In this section we report numerical values for the lattice terms W_j^{2n} appearing in M_8 and M_6 for the case of a simple-cubic lattice of identical spins. W_j^{2n} is dependent upon the number of neighbors interacting with a given spin and upon the direction of the external magnetic field $\vec{B}_0$.

The calculation of W_j^{2n} involves in principle summations over an infinite lattice. However, it is of interest to see how many neighbors to a given spin is required to produce a good approximation to M_8 and M_6. Accordingly, we place a cube around a given spin and consider for that spin only the interactions with the spins in the cube in the evaluation of W_j^{2n}. The cube has the length $2Lr_0$, where r_0 is the lattice parameter of the cubic unit cell and L is an integer. Each cube contains $(2L+1)^3-1$ spins interacting with the central spin. Since all spins are equivalent we may keep one of the indices fixed and drop the factor N^{-1} in the calculation of W_j^{2n}. It is seen from Eqs. (23) and (24) that W_j^{2n} consists of three types of lattice terms, involving 1 (for example, S_8), 2 [for example, $B_{jk}^6R_{jk}(11)$], and 3 [for example, $Q(221)$] summation indices, respectively. We have evaluated the lattice terms as a function of L. They are listed in Tables I and II. In this calculation we have reexpressed M_{2n} as

$$M_{2n}=\left(\frac{3\gamma^2\hbar}{2r_0^3}\right)^{2n}\sum_{j=1}^{n}W_j^{2n}X^j \quad (27)$$

to facilitate the comparison with other results.[3,11] Tables I and II demonstrate that the most important contribution to W_j^{2n} comes from sums involving one summation index and that the terms involving three indices play a negligible role only. This is in agreement with the conjecture made by Gade and Lowe[10,11] that the largest contribution to M_{2n} comes from terms involving $n+1$ spins, since the reduction of such terms will reduce to lattice sums such as S_2^n which are the largest of the terms appearing in M_8 and M_6. It should be pointed out that we get the same numerical (and analytical) results for M_4 and M_2 as found previously.[1] However, our numerical results for W_2^6 and W_3^6 for the magnetic field along the [100] direction do not agree with those reported by Glebashev.[12] The reason for this discrepancy is not obvious, as Glebashev lists

the numerical values of W_j^6 only.

All the computations have been performed on the CDC 6400 computer at RECAU, The Regional Computing Center at Aarhus University.

V. COMPARISON OF M_8 AND M_6 PREDICTED FROM ABRAGAM'S TRIAL FUNCTION WITH THE EXACT MOMENTS

Abragam[2] has proposed a trial function for the free-induction-decay curve [Eq. (4)] which is given by

$$F(t) = e^{-a^2t^2/2}\sin(bt)/(bt). \tag{28}$$

The parameters a and b are adjusted to give the correct values of M_4 and M_2 for the corresponding spectrum $G(\omega)$ [Eq. (3)]. The trial function has shown a remarkable ability to reproduce experimental data[3] (at least for short times), and it is therefore interesting to check the agreement of Abragam's M_8 and M_6 with the exact M_8 and M_6. M_8 and M_6 are found by expanding Eq. (28) as

$$\begin{aligned} F(t) = 1 &- (a^2+\tfrac{1}{3}b^2)t^2/2! + (3a^4+2a^2b^2+\tfrac{1}{5}b^4)t^4/4! \\ &- (15a^6+15a^4b^2+3a^2b^4+\tfrac{1}{7}b^6)t^6/6! \\ &+ (105a^8+140a^6b^2+42a^4b^4+4a^2b^6+\tfrac{1}{9}b^8)t^8/8! \\ &+ \cdots \end{aligned} \tag{29}$$

and comparing the expansion with the exact expression

$$F(t) = \sum_{n=0}^{\infty} \frac{(-1)^n M_{2n} t^{2n}}{(2n)!}. \tag{30}$$

The results are given in Table III for the case of a simple cubic lattice in the classical limit $I \to \infty$ and with the interaction restricted to 26 nearest neighbors. This table shows that Abragam's M_8 and M_6 are smaller on the average than the corresponding exact theoretical moments by 30% and 10%, respectively. The moments in Table III may be compared to those reported in Ref. 3. In Table IV we make the same comparison for a spin-$\frac{1}{2}$ system. In this case the number of neighbors interacting with a given spin was taken as 342 [i.e., $(2\times3+1)^3-1$] in order to obtain realistic values for M_3 and M_6 to be compared to experiments. Table IV shows that Abragam's M_8 and M_6 are smaller on the average than the exact moments by 15 and 3%, respectively.

VI. DISCUSSION

When this paper was in preparation two papers were published[7,8] which both deal with the sixth moment M_6. The first one by Cheng and Memory[7] (CM) reports M_6, and the second one by Wurzbach and Gade[8] (WG) presents the four-spin contribution ${}^4M_6$ to M_6. To facilitate the comparison of the results we write our M_6 without making the reductions leading to Eq. (24):

TABLE I. Numerical values for the lattice terms appearing in $M_8 = (3\gamma^2\hbar/2r_0^3)^8 \sum_{j=1}^{4} W_j^8 X^j$ for a simple cubic lattice. Each spin interacts with $(2L+1)^3-1$ neighbors. 1°, 2°, and 3° indicate the number of indices summed over.

Direction of $\vec{B}_0$	L	W_1^8 1°	W_2^8 1°	2°	1°	W_3^8 2°	3°	1°	W_4^8 2°	3°
[100]	1	−10.43	276.65	7.13	−2328.65	−296.70	−1.80	10 166.08	281.90	−4.79
[100]	2	−10.43	286.18	−4.60	−2545.99	−224.52	−2.89	12 042.23	462.48	−5.02
[100]	3	−10.43	288.06	−5.18	−2589.63	−220.23	−2.96	12 437.51	500.20	−5.93
[100]	4	−10.43	288.66	−5.33	−2603.53	−219.34	−2.95	12 564.68	512.68	−5.98
[100]	9	−10.43	289.14		−2614.91			12 669.15		
[100]	10	−10.43	289.16		−2615.27			12 672.44		
[110]	1	−0.0433	2.0354	0.0807	−28.1530	−3.6974	−0.0061	202.0494	5.1416	−0.2557
[110]	2	−0.0433	2.1634	0.0166	−33.2067	−3.8246	−0.0400	277.3864	20.9522	−0.3951
[110]	3	−0.0433	2.1888	0.0109	−34.2663	−3.7985	−0.0416	294.7940	24.4938	−0.4276
[110]	4	−0.0433	2.1968	0.0093	−34.6070	−3.7903		300.5033	25.6181	
[110]	9	−0.0433	2.2034		−34.8870			305.2379		
[110]	10	−0.0433	2.2036		−34.8958			305.3879		
[111]	1	-8×10^{-5}	0.012 99	0.003 35	−0.457 49	−0.113 78	−0.002 82	6.445 57	0.437 23	0.007 24
[111]	2	-8×10^{-5}	0.014 49	0.003 24	−0.630 17	−0.144 62	−0.003 83	12.001 82	1.310 00	0.017 94
[111]	3	-8×10^{-5}	0.014 78	0.003 17	−0.668 07	−0.144 44	−0.004 05	13.477 53	1.602 77	0.019 06
[111]	4	-8×10^{-5}	0.014 88	0.003 15	−0.680 38	−0.144 44		13.975 99	1.703 23	
[111]	9	-8×10^{-5}	0.014 95		−0.690 56			14.394 88		
[111]	10	-8×10^{-5}	0.014 95		−0.690 88			14.408 24		

TABLE II. Numerical values of the lattice terms appearing in $M_6=(3\gamma^2\hbar/2r_0^3)^6\sum_{j=1}^{3}W_j^6X^j$ for a simple cubic lattice. Each spin interacts with $(2L+1)^3-1$ neighbors. 1°, 2°, and 3° indicate the number of indices summed over.

Direction of $\vec{B}_0$	L	W_1^6 1°	W_2^6 1°	W_2^6 2°	W_3^6 1°	W_3^6 2°	W_3^6 3°
[100]	1	1.900	−54.326	−0.302	511.992	5.071	−0.052
[100]	2	1.900	−56.702	−0.729	579.710	26.193	0.020
[100]	3	1.900	−57.166	−0.749	593.615	29.465	0.012
[100]	4	1.900	−57.313	−0.754	598.063	30.431	0.011
[100]	9	1.900	−57.433		601.709		
[100]	10	1.900	−57.437		601.824		
[110]	1	0.0333	−1.6557	−0.0585	26.6857	0.9412	−0.0096
[110]	2	0.0333	−1.7943	−0.0733	33.7352	2.7374	−0.0103
[110]	3	0.0333	−1.8218	−0.0743	35.2901	3.1279	−0.0107
[110]	4	0.0333	−1.8305	−0.0746	35.7950	3.2519	
[110]	9	0.0333	−1.8377		36.2118		
[110]	10	0.0333	−1.8379		36.2249		
[111]	1	0.000 43	−0.060 47	−0.004 63	1.993 18	0.031 31	0.001 03
[111]	2	0.000 43	−0.071 07	−0.006 10	3.164 60	0.202 30	0.002 19
[111]	3	0.000 43	−0.073 14	−0.006 20	3.449 95	0.266 62	0.002 31
[111]	4	0.000 43	−0.073 81	−0.006 23	3.544 52	0.289 09	
[111]	9	0.000 43	−0.074 35		3.623 35		
[111]	10	0.000 43	−0.074 36		3.625 85		

$$M_6=\gamma^{12}\hbar^6N^{-1}\Big[28\,350^{-1}(2582X^3-1693X^2+408X)\sum_{j,k}{}' B_{jk}^6+2430^{-1}\Big((1220X^3-345X^2)\sum_{j,k,l}{}' B_{jk}^4B_{jl}^2$$
$$+(232X^3-9X^2)\sum_{j,k,l}{}' B_{jk}^4B_{jl}B_{kl}+(192X^3+6X^2)\sum_{j,k,l}{}' B_{jk}^3B_{jl}^2B_{kl}+(-80X^3+30X^2)\sum_{j,k,l}{}' B_{jk}^3B_{jl}^3$$
$$+(370X^3-120X^2)\sum_{j,k,l}{}' B_{jk}^2B_{jl}^2B_{kl}^2\Big)+729^{-1}X^3\Big(128\sum_{j,k,l,m}{}' B_{jk}^2B_{jl}^2B_{jm}^2+116\sum_{j,k,l,m}{}' B_{jk}^2B_{jl}^2B_{jm}B_{km}$$
$$-12\sum_{j,k,l,m}{}' B_{jk}^2B_{lm}^2B_{jl}B_{jm}+101\sum_{j,k,l,m}{}' B_{jk}^2B_{jl}^2B_{km}^2+84\sum_{j,k,l,m}{}' B_{jk}^2B_{jl}B_{jm}B_{kl}B_{km}+4\sum_{j,k,l,m}{}' B_{jk}^2B_{jl}B_{jm}B_{kl}B_{lm}$$
$$-32\sum_{j,k,l,m}{}' B_{jk}^2B_{lm}^2B_{jl}B_{km}+24\sum_{j,k,l,m}{}' B_{jk}^2B_{jl}^2B_{km}B_{lm}-8\sum_{j,k,l,m}{}' B_{jk}B_{jl}B_{jm}B_{kl}B_{km}B_{lm}\Big)\Big]\,. \quad (31)$$

Equation (31) contains the same fifteen lattice sums as obtained by CM [their Eq. (3.18)]. However, the numerical coefficients of the following seven lattice sums $B_{jk}^3B_{jl}^2B_{kl}$, $B_{jk}^3B_{jl}^3$, $B_{jk}^2B_{jl}^2B_{kl}^2$, $B_{jk}^2B_{jl}^2B_{jm}^2$, $B_{jk}^2B_{jl}^2B_{jm}B_{km}$, $B_{jk}^2B_{jl}B_{jm}B_{kl}B_{km}$, and $B_{jk}^2B_{jl}B_{jm}B_{kl}B_{lm}$ differ from those of CM. We have made a straightforward manual calculation of one of the above mentioned terms ($B_{jk}^2B_{jl}^2B_{jm}^2$), and this calculation confirms the result obtained with our computer program.

The four-spin terms of Eq. (31) are identical to those of WG except for the coefficient to $B_{jk}^2B_{lm}^2B_{jl}B_{jm}$, which WG find to be $-1/729$ whereas we get $-12/729$. We have also recalculated this term manually and again have confirmed the

TABLE III. Comparison of M_8 and M_6 predicted from Abragam's trial function (A) with the exact moments for a simple-cubic lattice (B). Each spin interacts with 26 neighbors and the moments are evaluated in the limit $I\to\infty$, $\hbar\to0$, while $I\hbar$ remains finite. M_{2n} is given in units of $(2r_0^3/3\gamma|\vec{\mu}|)^{-2n}$.

Direction of $\vec{B}_0$	M_8 A	M_8 B	M_6 A	M_6 B
[100]	7085.48	10 443.19	472.422	517.011
[110]	160.116	206.935	26.1075	27.6173
[111]	4.71962	6.890 04	1.846 76	2.025 52

TABLE IV. Comparison of M_8 and M_6 predicted from Abragam's trial function (A) with the exact moments (B) for a simple cubic lattice with spin-$\frac{1}{2}$. Each spin interacts with 342 neighbors ($L=3$). M_{2n} is given in units of $(2r_0^3/3\gamma^2\hbar)^{-2n}$.

Direction of $\vec{B}_0$	M_6 A	M_6 B	M_6 A	M_6 B
[100]	2614.86	3056.33	224.377	231.714
[110]	76.8808	86.0181	14.8532	15.1614
[111]	3.558 04	4.443 08	1.450 15	1.524 59

result of our computer program. Furthermore, CM get the same result as we do for this lattice term. Accordingly, we have reason to believe that our expressions are correct.

Thus, the moments reported here may serve to expand the basis for further theoretical developments in the field of magnetic-resonance line shapes of rigid lattices.

Note added in proof. Professor J. D. Memory [J. D. Memory (private communication)] has kindly informed us that he and Professor S. Gade [J. D. Memory and S. Gade, Phys. Rev. B (to be published)] have confirmed that the correct form of the sixth moment is the one presented here, Eq. (31).

APPENDIX

We want to outline a straightforward method for algebraic computer calculation of a trace of a product of angular momentum operators.

We consider a product K of n angular momentum operators, all operating on the same variables:

$$K = \prod_{j=1}^{n} I_{q_j}, \tag{A1}$$

where $q_j = x, y, z$. I_x, I_y, and I_z appear as factors n_x, n_y, and n_z times, respectively, in Eq. (A1).

I_x and I_y are expressed as

$$I_x = \tfrac{1}{2}(I_+ + I_-), \tag{A2}$$

$$I_y = \tfrac{1}{2} i (I_- - I_+). \tag{A3}$$

We substitute the right-hand side of Eqs. (A2) and (A3) for all the operators I_x and I_y in Eq. (A1). The trace of K may then be written

$$\mathrm{Tr}\, K = (\tfrac{1}{2})^{n_x+n_y} (i)^{n_y} \sum_{j=1}^{R'} (-1)^{b_j} \mathrm{Tr}\, K_j, \tag{A4}$$

where K_j is a product of the operators I_z, I_+, and I_-, b_j is the number of I_+ operators substituted for I_y in K_j, and $R' = 2^{n_x+n_y}$. Since $\mathrm{Tr}\, K_j$ is zero unless K_j contains equal numbers of factors of I_+ and I_-,[13] we may replace R' by

$$R = (n_x+n_y)! / \{[\tfrac{1}{2}(n_x+n_y)]!\}^2. \tag{A5}$$

We number the operators in K_j from the right and denote the kth operator as I_{s_k}, where s_k is the step value. I_z, I_+, and I_- have the step values $s_k = 0$, 1, and -1, respectively. Each operator is assigned a level number d_k defined as

$$d_k = \sum_{j=1}^{k-1} s_j, \tag{A6}$$

$$d_1 = 0. \tag{A7}$$

The trace of K_j may now be written

$$\mathrm{Tr}\, K_j = \sum_{m=-I}^{I} \langle m | \prod_{p=1}^{n} I_{s_p} | m \rangle = \sum_{m=-I}^{I} \prod_{p=1}^{n} \langle m + d_{p+1} | I_{s_p} | m + d_p \rangle, \tag{A8}$$

where we have set $d_{n+1} = 0$. We note that if the operator $I_{s_{k_1}}$ is I_1 then we can find an operator $I_{s_{k_{-1}}} = I_{-1}$ such that

$$d_{k_{-1}} = d_{k_1} + 1. \tag{A9}$$

The product of the matrix elements of the k_1th and k_{-1}th operators is

$$\langle m + d_{k_{-1}} - 1 | I_{-1} | m + d_{k_{-1}} \rangle \langle m + d_{k_1} + 1 | I_1 | m + d_{k_1} \rangle = I(I+1) - (m + d_{k_1} + 1)(m + d_{k_1}), \tag{A10}$$

where we have used Eq. (A9) and the relation

$$I_{\pm 1} | m \rangle = [I(I+1) - m(m \pm 1)]^{1/2} | m \pm 1 \rangle. \tag{A11}$$

We may now write Eq. (A8) as

$$\mathrm{Tr}\, K_j = \sum_{m=-I}^{I} \left(\prod_{k_0} (m + d_{k_0}) \right) \times \left(\prod_{k_1} [X - (m + d_{k_1} + 1)(m + d_{k_1})] \right), \tag{A12}$$

where $X = I(I+1)$. In Eq. (A12) we have collected all matrix elements of $I_0 (s_k = 0)$ into one product and all matrix elements of pairs of $I_1 (s_k = 1)$ and $I_{-1} (s_k = -1)$ into another product. Carrying out the multiplication in Eq. (A12) we obtain

$$\mathrm{Tr}\, K_j = \sum_p A_{2p} \sum_{m=-I}^{I} m^{2p}, \tag{A13}$$

where A_{2p} contains X and the level numbers. $\sum_{m=-I}^{I} m^{2p}$ may be found in Ref. 14.

Accordingly, the computer calculation requires a representation of the product of the angular momentum operators [Eq. (A1)], which is split into a sum of products K_j of operators I_0, I_1, and I_{-1} [Eq. (A4)]. The computer assigns level numbers to the operators in each K_j, determines the pairs of I_1 and I_{-1}, and evaluates the product in Eq. (A12). The final step requires substituting the expression for $\sum_{m=-I}^{I} m^{2p}$.

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PHYSICAL REVIEW B VOLUME 7, NUMBER 7 1 APRIL 1973

Linear Electric Field Effect in Paramagnetic Resonance for Nd^{3+} and U^{3+} Tetragonal Sites in Fluorite Lattices

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(Received 16 November 1972)

We have made a comparative study of the electric-field-induced g shifts in paramagnetic resonance for tetragonal Nd^{3+} sites in CaF_2 and SrF_2, and for tetragonal U^{3+} sites in CaF_2, SrF_2, and BaF_2. Approximate estimates for the shifts in CaF_2 are given, and the variation of the shifts through the series of host lattices is discussed.

I. INTRODUCTION

We have made a comparative study of the linear electric field shifts in paramagnetic resonance for the ions Nd^{3+} ($4f^3$) and U^{3+} ($5f^3$) in C_{4v} F^- charge-compensated sites in the fluorite lattice. U^{3+} has been studied in CaF_2, SrF_2, and BaF_2 and Nd^{3+} in CaF_2 and SrF_2. Measurements were not made for Nd^{3+} in BaF_2 since the tetragonal sites could not be found in this material.

II. EXPERIMENTAL

The measurements were made by the electron-spin-echo method at a frequency of 9.4 GHz and at a temperature of 4.2°K. As in an earlier study of Ce^{3+} involving fluorite host lattices,[1] the observations proved to be difficult to make because of deep nuclear modulation of the echo envelope and short phase-memory times. The U^{3+} samples showed particularly striking modulation effects, including inversion of the echo signals. Because of these difficulties the accuracy was not as good as that which is usually attainable by the spin-echo method.

The electric field effects for Kramers-doublet ions in C_{4v} sites can be fitted by the relation

$$\delta(g^2) = E_\perp B_{15} \sin 2\theta + E_\parallel (B_{31} \sin^2\theta + B_{33} \cos^2\theta), \quad (1)$$

where $E_\parallel$, $E_\perp$ are electric fields applied parallel and perpendicular to the C_{4v} axis and θ is the angle between the Zeeman field and this axis.[2] The parameters B_{ij} are related to the T_{ij} in the electric effect Hamiltonian

$$\mathcal{H}_{\text{elec}} = E_x T_{15}(H_x S_z + H_z S_x) + E_y T_{15}(H_y S_z + H_z S_y) + E_z[T_{31}(H_x S_x + H_y S_y) + T_{33} H_z S_z] \quad (2)$$

by the equations

$$B_{15} = T_{15}(g_\parallel + g_\perp), \quad B_{31} = 2T_{31} g_\perp, \quad B_{33} = 2T_{33} g_\parallel . \quad (3)$$

The z axis is here the C_{4v} axis; the x and y axes lie in the perpendicular plane.

The results are given in Table I in units of g^2 shift per 10^9-V/cm applied field. The absolute signs of the B_{ij} could not be determined, but it was verified that B_{31} and B_{33} were of opposite sign. The g values for the CaF_2 and SrF_2 lattices are those given by Bleaney, Llewellyn, and Jones.[3] The g values for U^{3+} in BaF_2 were determined during the present work.

TABLE I. g values and linear electric-field-effect parameters for F^- compensated tetragonal Nd^{3+} and U^{3+} sites in fluorite lattices. The B_{ij} give changes in g^2 per 10^9 V/cm of applied field [Eq. (1)] and are related to the g-shift parameters T_{ij} [Eqs. (2) and (3)].

	$g_\parallel$	$g_\perp$	B_{33}	B_{31}	B_{15}
$CaF_2:Nd^{3+}$	4.412[a] ± 0.008	1.301[a] ± 0.002	133 ± 13	−17 ± 2	181 ± 18
$SrF_2:Nd^{3+}$	4.289[a] ± 0.008	1.505[a] ± 0.002	210 ± 22	−47 ± 9	230 ± 23
$CaF_2:U^{3+}$	3.501[a] ± 0.008	1.866[a] ± 0.002	48 ± 5	−28 ± 3	213 ± 21
$SrF_2:U^{3+}$	3.433[a] ± 0.008	1.971[a] ± 0.002	34 ± 4	−22 ± 4	275 ± 27
$BaF_2:U^{3+}$	3.233[b] ± 0.008	2.108[b] ± 0.002	78 ± 8	−35 ± 6	350 ± 35

[a]From Ref. 3. [b]From present measurements.