Third moment of an NMR spectrum in a rotating frame

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Our previously derived expression for the third moment of an NMR spectrum in a rotating frame is supplemented by a new term containing lattice sums with a smaller number of summation indices. The spectrum of a model system in which the spins interact equally with one another is found in order to verify the final result. © *1995 American Institute of Physics.*

One of the fundamental problems of nuclear magnetic resonance (NMR) in solids is the calculation of the absorption line shape (the spectrum). The interaction determining its form, i.e., the dipole–dipole interaction for traditional NMR[1] or the effective interaction created from the dipolar interaction by a strong radio-frequency (rf) field in the case of NMR in a rotating frame,[2,3] ultimately couples all the spins in the system to one another. Therefore, this many-particle problem does not have an exact solution. However, exact expressions can be obtained for integrated characteristics of the spectra, viz., the moments M_n (Ref. 1), at least for the first few. The first moment M_1 characterizes the position of the center of a line, M_2 describes its width, and M_3 specifies its asymmetry. Moments have played an important role in devising the theory of the line shape, since, first, they are used, first to verify the expressions obtained is verified on their basis and, second, to determine the parameters in approximate equations.

The complexity of the calculation increases very rapidly with increasing order of the moment. In NMR in a rotating frame the difficulties are heightened by the fact that the effective interaction is a three-spin interaction. Therefore, while the moments have been calculated up to the eighth order inclusively in conventional NMR,[4] only M_1 and M_2 are known in a rotating frame.[2,3,5] We recently derived an expression for the third moment.[6] Zaĭtsev and Sabirov presented their expression in Ref. 7. The results do not coincide. In the present work we find the NMR spectrum in a rotating frame for a model system in which each spin interacts equally with all the other spins.[8] It is used to verify the coefficients in front of the various lattice sums and to obtain an exact analytical expression for the third moment. The lattice sums and the numerical value of M_3 are calculated for a simple cubic lattice.

To begin, we consider a system of N spins ($S=1/2$) interacting equally with one another in a strong constant field and a strong rf field. The effective Hamiltonian in the rotating frame[2,3,5,6] consists of one- ($\hat{\mathscr{H}}_1$), two- ($\hat{\mathscr{H}}_2$), and three-spin ($\hat{\mathscr{H}}_3$) interactions. Here $\hat{\mathscr{H}}_1$ expresses the shift of the mea[illegible]ion frequency in the effective field, which we include in its value (ω_e). We transform the other two parts so as to express them in terms of the components of the vector operator of the total spin of the system $\{\hat{S}_x,\hat{S}_y,\hat{S}_z\}$:

$$\hat{\mathscr{H}}_2=3mb(\hat{S}_z^2-\sigma^2)/2,$$

$$\hat{\mathscr{H}}_3=A\{(2c-s)\hat{S}_z\hat{S}^2-(4c-s)\hat{S}_z^3+2\sigma^2\hat{S}_z(c+s)-c\hat{S}_z\},\tag{1}$$

where $\hat{S}^2=\hat{S}_x^2+\hat{S}_y^2+\hat{S}_z^2$, $m=(3\cos^2\theta-1)/2$, $c=\sin^2 2\theta$, $s=\sin^4\theta$, $\sigma^2=N/4$, $A=9b^2/(16\omega_e)$, b is the dipole coupling constant, and θ is the angle between the directions of the effective field (the z axis) and the constant magnetic field.

The eigenfunctions of the Hamiltonian (1) are eigenfunctions of the total spin of the system and its z projection, which are characterized by the pair of quantum numbers (S,S_z). The eigenstates with assigned values of (S,S_z) are multiply degenerate. For example, the degeneracy multiplicity for even N is expressed as the difference between two binomial coefficients:[8]

$$g(S,S_z)=g(S)=\binom{N}{N/2-S}-\binom{N}{N/2-S-1}.\tag{2}$$

Transitions caused by a resonant field which is orthogonal to the effective field[3] (with operator $\hat{S}_-=\hat{S}_x-i\hat{S}_y$) occur between states with identical values for the total spin and values of S_z differing by unity. The transition between the (S,S_z+1) and (S,S_z) states produces a line in the spectrum with a frequency measured relative to ω_e

$$\Omega(S,S_z)=3mb(2S_z+1)/2+A\{(2c-s)S(S+1)-(4c-s)(3S_z^2+3S_z+1)+2\sigma^2(c+s)-c\}\tag{3}$$

and an intensity

$$P(S,S_z)=g(S,S_z)(S+S_z+1)(S-S_z)/C,\tag{4}$$

where $C=\mathrm{Tr}\{\hat{S}_-\hat{S}_+\}=N\cdot 2^{N-1}$ is a normalization factor.

The simplest system which exhibits the interaction $\hat{\mathscr{H}}_3$ is a system of three spins. Its spectrum consists of four lines with the frequencies

$$\Omega(\tfrac{3}{2},-\tfrac{3}{2})=-A(5c-s)-3mb,$$

$$\Omega(\tfrac{3}{2},\tfrac{1}{2})=-A(5c-s)+3mb,$$

$$\Omega(\tfrac{1}{2},-\tfrac{1}{2})=A(c+s),\quad \Omega(\tfrac{3}{2},-\tfrac{1}{2})=A(7c-2s),$$

and with the intensities

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$$P(\tfrac{3}{2},-\tfrac{3}{2})=1/4, \quad P(\tfrac{3}{2},\tfrac{1}{2})=1/4,$$

$$P(\tfrac{1}{2},-\tfrac{1}{2})=1/6, \quad P(\tfrac{3}{2},-\tfrac{1}{2})=1/3.$$

The moments of the spectrum are determined from the formula

$$M_n=\tfrac{1}{4}\Omega^n(\tfrac{3}{2},-\tfrac{3}{2})+\tfrac{1}{4}\Omega^n(\tfrac{3}{2},\tfrac{1}{2})+\tfrac{1}{6}\Omega^n(\tfrac{1}{2},-\tfrac{1}{2})+\tfrac{1}{3}\Omega^n(\tfrac{3}{2},-\tfrac{1}{2}).$$

In particular,

$$M_2=A^2(29c^2-14cs+2s^2)+(3mb)^2/2, \tag{5}$$

$$M_3=-3A(3mb)^2(5c-s)/2+A^3(52c^3-60c^2s+21cs^2-2s^3). \tag{6}$$

Equations (2)–(4) specify the spectrum for $N=4$, etc. We proceed at once to the case of large N, since the limit $N\rightarrow\infty$ makes it possible to isolate the contribution of the lattice sums with the largest number of summations to the moments. In this case, instead of calculating the spectrum itself, it is convenient to calculate its Fourier transform, i.e., the free-precession signal, in the rotating frame:

$$\mathcal{M}(t)=\mathrm{Tr}\{\exp(i\hat{\mathcal{H}}t)\hat{S}_-\exp(-i\hat{\mathcal{H}}t)\hat{S}_+\}/\ \mathrm{Tr}\{\hat{S}_-\hat{S}_+\}. \tag{7}$$

Taking the eigenfunctions of the Hamiltonian (1) as a basis and using Eqs. (2)–(4), we obtain from (7)

$$\mathcal{M}(t)=\sum_{S=0}^{N/2}\sum_{S_z=-S}^{S}P(S,S_z)\exp\{it\Omega(S,S_z)\}. \tag{8}$$

Equation (8) describes systems of an arbitrary number of spins. It can be simplified significantly in the limit of large N. Let us, first of all, determine the order of magnitude with respect to N of the various contributions to the frequency $\Omega(S,S_z)$. In the high-temperature limit under consideration the mean value of the components of the total spin vanishes, while for their squares we find

$$\langle S_\alpha^2\rangle=\mathrm{Tr}(S_\alpha^2)/\mathrm{Tr}\ 1=\sigma^2=N/4 \quad (\alpha=x,y,z).$$

Therefore, the first term in (3) is of order $N^{1/2}$. The second term in (3) is of the same order, since the increase in the power of S_α in it is compensated by the factor $\omega_e\propto N^{1/2}$ in the denominator of the coefficient A. The amplitude of the effective field is determined by the amplitude of the mean local field from the dipolar interaction, which it must exceed in order to cause narrowing of the NMR line in the rotating frame.

According to the evaluations performed, when only the principal terms with respect to N are retained in Eqs. (2)–(4), from (8) we obtain

$$\mathcal{M}(t)=\int_{-\infty}^{\infty}dS_z\int_{|S_z|}^{\infty}dS\ P(S,S_z)\exp\{it\Omega(S,S_z)\}, \tag{9}$$

where

$$P(S,S_z)=S(S^2-S_z^2)\exp\left(\frac{-S^2}{2\sigma^2}\right)\frac{1}{\sqrt{8\pi\sigma^5}},$$

$$\Omega(S,S_z)=-a_zS_z^2+a_\perp S_\perp^2+3mbS_z+\Omega_0,$$

$$a_z=2A(5c-s), \quad a_\perp=A(2c-s),$$

$$\Omega_0=(a_z-4a_\perp)\sigma^2=2A\sigma^2(c+s),$$

Performing the integration, we find

$$\mathcal{M}(t)=\exp\left[-\frac{1}{2}\frac{t^2(3mb)^2\sigma^2}{1+2ita_z\sigma^2}+it\Omega_0\right]\times\frac{1}{\sqrt{1+2ita_z\sigma^2}(1-2ita_\perp\sigma^2)^2}. \tag{10}$$

The desired moments can be obtained[1] by expanding (10) in powers of the time:

$$M_2=(3mb)^2\sigma^2+2\sigma^4(a_z^2+4a_\perp^2), \tag{11}$$

$$M_3=-6\sigma^4(3mb)^2a_z-8\sigma^6(a_z^3-4a_\perp^3). \tag{12}$$

We now take the expression which we presented in Ref.6 for M_3 in real systems, and we replace the b_{ij} by b in the lattice sums. As result we obtain $P_1=P_2=L_1=L_2=L_3=L_4=L_5=L_6=1$ and

$$M_3^{DE}=-3Km^2(M_2^0)^{3/2}(5c-s)/4,$$

$$M_3^{EE}=-4^{-4}\cdot 2K^3(M_2^0)^{3/2}(242c^3-137c^2s+24cs^2-s^3).$$

These expressions are identical with the corresponding expressions (12), since $M_2^0=9Nb^2/4=9b^2\sigma^2$ and $K^2=9b^2\sigma^2/\omega_e^2$. It is easy to prove that the expressions for M_2 coincide.

Zaĭtsev and Sabirov[7] presented an expression for M_3 when $\theta=\theta_M=54°44'$, from which we find $|M_3/M_2^{3/2}|=1.8$ when $b_{ij}=b$, while a value of 2.37 follows from (11) and (12). The relation between the coefficients in the different lattice sums with four lattice indices is illustrated by the ratio between the corresponding contributions ($^4M_3$) from the two papers

$$-\frac{^4M_3(\mathrm{Ref.6})}{^4M_3(\mathrm{Ref.7})}=3\frac{77L_1+339L_2+108(L_3+L_4)+282L_5+40L_6}{167L_1+743L_2+259L_3+210L_4+705L_5+9fL_6},$$

where we are obliged to copy the coefficient in front of L_6 from Ref. 7 together with the f.

On the other hand, since M_2 and M_3^{DE} (Ref. 6) are expressed in terms of lattice sums with three indices, these contributions can be compared with the results (5) and (6) for a three-spin system. In this system $M_2^0=9b^2/2$, $P_1=P_2=1/2$, and we obtain agreement between the results.

In addition to M_3^{DE}, (6) contains another contribution, which we did not take into account in Ref. 6. After performing the necessary calculations in the general case, we obtained the following expression for it:

$$^3M_3^{EE}=4^{-4}K^3(M_2^0)^{3/2}\{6c(2c^2-2cs+s^2)Q_1+(23c^3-27c^2s+9cs^2-s^3)(3Q_2+Q_3)\}, \tag{13}$$

where $M_2^0=9B/4$, $K^2=M_2^0/\omega_e^2$, and we have introduced the lattice sums

$$Q_1=\frac{1}{NB^3}\sum b_{ij}^3 b_{ik}^3,\quad Q_2=\frac{1}{NB^3}\sum b_{ij}^3 b_{ik}^2 b_{kj},$$

$$Q_3=\frac{1}{NB^3}\sum b_{ij}^2 b_{ik}^2 b_{jk}^2,\quad B=\frac{1}{N}\sum b_{ij}^2,$$

in which the summation is carried out over all the indices, except those which coincide. This term did not make a contribution to (12), since it is smaller than ${}^4M_3^{EE}$ by a factor of order N due to the smaller number of summation indices in the lattice sums. Although the sums P_1 and P_2 in the contribution from M_3^{DE} (Ref. 6) retained in (12) also have three summation indices, a smaller power of ω_e appears in front of them in the denominator of the coefficient.

For a system of three spins with an equal interaction $B=2b^2$, we find $Q_1=Q_2=Q_3=1/4$, and (13) is transformed into (6).

A contribution similar to (13) can be distinguished in the expression for M_3 in Ref. 7. The coefficients in front of Q_2 and Q_3 coincided with those obtained in (13) when $\theta=\theta_M$, while the coefficient in front of Q_1 turned out to be four times larger.

We calculated the lattice sums appearing in (13) for the case of a simple cubic lattice by summing over the spins located around the specified spin in a cube with an edge equal to 12 lattice constants for three orientations of the constant magnetic field relative to the crystallographic axes. The results are presented in Table I. The table also presents our calculated values of the ratio of the total third moment for $\theta=\theta_M$, i.e., $M_3={}^4M_3^{EE}+{}^3M_3^{EE}$ to $M_2^{3/2}$, which decreased by 4% in the [100] orientation and by 1% in the other two orientations after the contribution of ${}^3M_3^{EE}$ was taken into account. (The calculation in the [111] orientation was performed with refined lattice sums: $P_2=0.141$, $L_1=0.871$, $L_2=0.132$). When θ deviates from θ_M, the relative contribution of ${}^3M_3^{EE}$ decreases rapidly as a consequence of the increase in M_3^{DE}. This refinement of M_3 scarcely alters the results of the calculation of the free-precession signal in a rotating frame in CaF_2. Conversely, in systems with a small number of neighbors, for example, systems consisting of quasi-isolated groups or one-dimensional chains, the proportion of the ${}^3M_3^{EE}$ contribution can increase, and it can no longer be disregarded.

TABLE I.

	$-M_3/M_2^{3/2}$	$Q_1\cdot 10^2$	$Q_2\cdot 10^2$	$Q_3\cdot 10^2$
[100]	0.71	0.408	1.125	0.650
[110]	0.96	−1.203	0.626	1.041
[111]	1.04	−0.148	0.223	1.008

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