Dipolar Broadening of the Quadrupole Resonance Line Width in Zero Applied Field

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A formula has been derived for the contribution of the dipolar broadening to the second moment of the resonance line in pure quadrupole resonance experiments.

The following assumptions have been made: The nuclear spins undergoing the resonant transitions have spin 1 or $\frac{3}{2}$. No restriction has been set on the spins of "nonresonant" nuclei contributing to the dipolar broadening. The electric field gradients at all nuclear sites have axial symmetry and common directions.

A comparison is made with Van Vleck's formula for straight magnetic resonance.

INTRODUCTION

VAN Vleck[1] has shown that the second moment of a magnetic resonance line is given by the formula

$$\langle h^2\nu^2\rangle_{\mathrm{Av}}=-\mathrm{Tr}[H, S_x]^2/\mathrm{Tr}(S_x)^2. \quad (1)$$

H is the Hamiltonian of a system of spins including their mutual dipole-dipole interaction, and S_x is the component along the direction of the applied rf field, of the total spin of the resonant system.

As Van Vleck points out, there are certain precautions to be taken in using Eq. (1). The Hamiltonian H can be broken up into two parts, H_0 which is the sum of the energies of the individual spins, neglecting their mutual interactions, and H_1 which is the sum of these interactions and is generally much smaller than H_0. H_1 in turn can be split into two parts $H_1=H_1'+H_1''$ in the following way. H_1' is the part of H_1 which commutes with H_0. In a representation where H_0 is diagonal, H_1' has no off-diagonal elements. H_1'' is defined by the condition that in the same representation it has no diagonal matrix elements. The effect of H_1' is to broaden the sharp resonance line which would obtain in the absence of interactions. On the other hand, H_1'' produces weak satellite lines by mixing together eigenstates of H_1 of different energy.

In a resonance experiment the satellite lines are of no interest and only the so-called "truncated" Hamiltonian $\bar{H}=H_0+H_1'$ should be used in Eq. (1), instead of H, to calculate the second moment of the main line. The same caution must be exercised in the use of S_x in order to insure that only transitions corresponding to the main line are considered. Matrix elements of S_x corresponding to other transitions should be discarded and a "truncated" operator $\bar{S}_x$ used in Eq. (1) instead of S_x. The breakup of the interaction H_1 in its two components H_1' and H_1'', and thence the value of the second moment, depends on the form of H_0. Different cases have been considered by several authors.

Van Vleck[1] has applied Eq. (1) to the case of straight magnetic resonance in a magnetic field. Van Vleck and Ollom,[2] Ishiguro, Kambe, and Usui,[3] and Stevens[4] have considered the case of a crystalline electric field superimposed on the external magnetic field. They have considered a paramagnetic ion of spin one, but the treatment is the same as for a nucleus of spin one with a quadrupole moment. Bersohn[5] has considered the case where the Stark or quadrupole splittings are so small that they are on a par with the dipole-dipole interactions in broadening the resonance line observed in an external magnetic field. Pryce and Stevens[6] have given a general theory of magnetic resonance line width which covers practically all possible cases of dipolar broadening but by their very generality their formulas are ill adapted to a direct comparison with experiment.

The purpose of the present article is to give explicit expressions for the second moment of the resonance line in the important case of "pure quadrupole resonance" or of resonance transitions between different quadrupole levels in the absence of an external magnetic field. Some of the results have been reported previously.[7] The principle rather than the details of the calculations is given.

The treatment depends on whether the nuclei undergoing the resonant transitions or "resonant" nuclei interact among themselves or with different "nonresonant" nuclei. We shall consider the two cases separately. Since the second moments are additive this is not a restriction of generality. The complexity of the calculations increases rapidly with increasing value of the spin of the resonant nuclei. We have considered the cases of resonant nuclei of spin 1 and $\frac{3}{2}$. No restriction has been set on the spins of the nonresonant nuclei.

Case I. Interaction between Resonant Nuclei Only

We assume that the interacting nuclei have identical quadrupole moments and are experiencing axial electric field gradients of common directions and magnitudes. The case of "semi-like" nuclei for which the gradient of the electric field has the same magnitude but different directions is much more involved and will not be considered here.

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[6] M. H. L. Pryce and K. W. H. Stevens, Proc. Phys. Soc. (London) **63**, 36 (1950).
[7] K. Kambe and A. Abragam, Phys. Rev. **90**, 348 (1953).

The unperturbed Hamiltonian H_0 can be written as

$$H_0=-\delta\sum_i S_{zi}^2, \tag{2}$$

where z is the axis of symmetry of the electric field and S_{zi} the z component of the spin of the ith nucleus. δ is a parameter proportional to the strength of the quadrupole interaction. The resonance frequencies are $\nu_0=\delta/h$ and $\nu_0=2\delta/h$ for spin 1 and $\frac{3}{2}$, respectively. The interaction Hamiltonian H_1 responsible for the dipolar broadening can be written with the usual notation:

$$\begin{aligned}H_1=\sum_{j>k}W_{jk}&=g^2\beta^2\sum_{j>k}r_{jk}^{-3}\{(\mathbf{S}_j\cdot\mathbf{S}_k)\\&\quad-3r_{jk}^{-2}(\mathbf{S}_j\cdot\mathbf{r}_{jk})(\mathbf{S}_k\cdot\mathbf{r}_{jk})\}\\&=g^2\beta^2\sum_{j>k}r_{jk}^{-3}\{(1-3\gamma_{jk}^2)S_{zj}S_{zk}\\&\quad-\tfrac{1}{4}(1-3\gamma_{jk}^2)(S_{+j}S_{-k}+S_{-j}S_{+k})\\&\quad-\tfrac{3}{2}\gamma_{jk}\eta_{jk}^-(S_{zj}S_{+k}+S_{+j}S_{zk})\\&\quad-\tfrac{3}{2}\gamma_{jk}\eta_{jk}^+(S_{zj}S_{-k}+S_{-j}S_{zk})\\&\quad-\tfrac{3}{4}(\eta_{jk}^-)^2S_{+j}S_{+k}-\tfrac{3}{4}(\eta_{jk}^+)^2S_{-j}S_{-k}\},\end{aligned} \tag{3}$$

where α_{jk}, β_{jk}, γ_{jk} are the direction cosines of r_{jk} with respect to the crystalline electric field axis; $\eta_{jk}^{\pm}=\alpha_{jk}\pm i\beta_{jk}$. As explained in the introduction, we must separate from the interaction Hamiltonian H_1 the part H_1' solely responsible for the broadening of the resonance line. Since the interactions W_{jk} are of the two body type, it is sufficient to consider two particular nuclei j and k. The unperturbed energy levels of this two-spin system are determined by the eigenvalues of the operator

$$-\delta(S_{zj}^2+S_{zk}^2). \tag{4}$$

A state of the two-spin system will be specified by the values m_j and m_k of S_{zj} and S_{zk} and denoted by (m_j, m_k). Matrix elements of the interaction W_{jk} connecting different energy levels of Eq. (4) must be discarded. This can be realized in two different ways.

In the first method, W_{jk} is modified by the introduction of suitable projection operators constructed analytically from the spin operators of the nuclei j and k. In the second method, the matrix elements of W_{jk} are written explicitly in numerical forms in a simple representation and those connecting different energy levels of Eq. (4) are discarded. The first method has been applied to the case of spin one as explained below but proved impracticable for the spin $\frac{3}{2}$ where the second method had to be used. The latter has also been used to check the results obtained for spin one by the first method.

Let us consider first the case of spin one. The energy levels and eigenstates of Eq. (4) are given in Table I. From an inspection of Table I and formula (3) we deduce the changes to make in W_{jk}. The first term of Eq. (3) is diagonal in the representation (m_j, m_k) and therefore should be retained unchanged. The second term has matrix elements between the states $(1,0)\leftrightarrow(0,1)$ and $(-1,0)\leftrightarrow(0,-1)$ which should be retained and matrix elements between $(0,0)\leftrightarrow(1,-1)$ and $(0,0)\leftrightarrow(-1,1)$ which should be discarded. This can be done by replacing in Eq. (3) $(S_{+j}S_{-k}+S_{-j}S_{+k})$ by $(S_{zj}+S_{zk})(S_{+j}S_{-k}+S_{-j}S_{+k})(S_{zj}+S_{zk})$. The third and fourth terms of Eq. (3) have matrix elements between different energy levels of Eq. (4) only and must be discarded altogether. The fifth and sixth terms have matrix elements $(1,0)\leftrightarrow(0,-1)$ and $(0,1)\leftrightarrow(-1,0)$ which must be retained and $(0,0)\leftrightarrow(-1,-1)$, $(0,0)\leftrightarrow(1,1)$ which must be discarded. This is realized by replacing in Eq. (3) $S_{+j}S_{+k}$ and $S_{-j}S_{-k}$, respectively by $-(S_{zj}+S_{zk})(S_{+j}S_{+k})(S_{zj}+S_{zk})$ and $-(S_{zj}+S_{zk})(S_{-j}S_{-k})(S_{zj}+S_{zk})$. The truncated Hamiltonian $\bar{H}=H_0+H_1'$ can be written as

TABLE I. Energy levels and eigenstates of two-spin system. Spin $S=1$.

Energies	States			
0	(0, 0)			
$-\delta$	(1, 0)	(0, 1)	(−1, 0)	(0, −1)
-2δ	(1, 1)	(1, −1)	(−1, 1)	(−1, −1)

$$\bar{H}=H_0+\sum_{j>k}\bar{W}_{jk}, \tag{5}$$

where

$$\begin{aligned}\bar{W}_{jk}=g^2\beta^2r_{jk}^{-3}[&(1-3\gamma_{jk}^2)S_{zj}S_{zk}\\&-\tfrac{1}{4}(1-3\gamma_{jk}^2)(S_{zj}+S_{zk})\\&\times(S_{+j}S_{-k}+S_{-j}S_{+k})(S_{zj}+S_{zk})\\&+\tfrac{3}{4}(S_{zj}+S_{zk})\{(\eta_{jk}^-)^2S_{+j}S_{+k}\\&+(\eta_{jk}^+)^2S_{-j}S_{-k}\}(S_{zj}+S_{zk})].\end{aligned} \tag{6}$$

Expressions (5) and (6) have to be used in Eq. (1) to calculate the second moment. Table I also shows that the operator $S_x=\sum_i S_{xi}$ connects states with energy difference δ only and can be used in Eq. (1) without modifications.

The calculation of the trace involved in Eq. (1) is very tedious but perfectly straightforward and leads to the following expression for the second moment:

$$\begin{aligned}S=1:\quad\langle h^2\Delta\nu^2\rangle_{\mathrm{Av}}&=\tfrac{1}{4}\sum_k g^4\beta^4r_{jk}^{-6}\\&\times[5(1-3\gamma_{jk}^2)^2+9(1-\gamma_{jk}^2)^2\\&\quad-2(1-3\gamma_{jk}^2)(\alpha_{jk}^2-\beta_{jk}^2)].\end{aligned} \tag{7}$$

For the spin $\frac{3}{2}$ case, as stated before, we write the matrix elements of W_{jk} explicitly. We choose a representation in which the basic states are $\{(m_j, m_k)\pm(m_k, m_j)\}/\sqrt{2}$ rather than (m_j, m_k) if $m_j\neq m_k$. The principal Hamiltonian, Eq. (4), as well as the interaction Hamiltonian W_{jk} being invariant through interchange of spins j and k, this choice of basic states reduces considerably the number of matrix elements of W_{jk}, since there are no matrix elements between odd

and even states. There are 16 states of the two-spin system, 10 even and 6 odd, and three energy levels $-\delta/2$, $-5\delta/2$, $-9\delta/2$.

The level $-\delta/2$ corresponds to a three-dimensional manifold $\mathcal{E}_1$ of even states and a one-dimensional manifold $\mathfrak{D}_1$ of odd states, the level $-5\delta/2$ to a four-dimensional even manifold $\mathcal{E}_2$ and a four-dimensional odd manifold $\mathfrak{D}_2$, and the level $-9\delta/2$ to a three-dimensional even manifold $\mathcal{E}_3$ and a one-dimensional odd manifold $\mathfrak{D}_3$. W_{jk} has matrix elements inside each manifold as well as between different manifolds of the same parity. The latter elements must be suppressed in order to obtain the "truncated" interaction W_{jk}. W_{jk} is then represented by the matrix (8):

$$\left[\begin{array}{ccc:ccc} E_1 & 0 & 0 & & & \\ 0 & E_2 & 0 & & 0 & \\ 0 & 0 & E_3 & & & \\ \hdashline & & & D_1 & 0 & 0 \\ & 0 & & 0 & D_2 & 0 \\ & & & 0 & 0 & D_3 \end{array}\right] \tag{8}$$

E_1, E_2, E_3 are square submatrices which correspond to the manifolds $\mathcal{E}_1$, $\mathcal{E}_2$, $\mathcal{E}_3$, and D_1, D_2, D_3 correspond to $\mathfrak{D}_1$, $\mathfrak{D}_2$, $\mathfrak{D}_3$. If now we write the matrix elements of S_x in the same representation, we find matrix elements

TABLE II. Various cases of dipolar broadening by nonresonant nuclei.

Case	Resonant spin S	Nonresonant spin S'
A_1	1	arbitrary (no quadrupole splitting)
A_2	1	half-integer (with quadrupole splitting)
A_3	1	integer (with quadrupole splitting)
B_1	$\frac{3}{2}$	arbitrary (no quadrupole splitting)
B_2	$\frac{3}{2}$	half-integer (with quadrupole splitting)
B_3	$\frac{3}{2}$	integer (with quadrupole splitting)

inside each manifold as well as between different manifolds of same parity. As explained in the introduction, we must keep only those connecting states with energy difference equal to the resonance energy, that is those connecting $\mathcal{E}_1 \leftrightarrow \mathcal{E}_2$, $\mathcal{E}_2 \leftrightarrow \mathcal{E}_3$, $\mathfrak{D}_1 \leftrightarrow \mathfrak{D}_2$, $\mathfrak{D}_2 \leftrightarrow \mathfrak{D}_3$. When this is done, the truncated operator $\bar{S}_x$ is represented by the matrix (9):

$$\left[\begin{array}{ccc:ccc} 0 & M_1 & 0 & & & \\ \bar{M}_1 & 0 & M_2 & & 0 & \\ 0 & \bar{M}_2 & 0 & & & \\ \hdashline & & & 0 & N_1 & 0 \\ & 0 & & \bar{N}_1 & 0 & N_2 \\ & & & 0 & \bar{N}_2 & 0 \end{array}\right] \tag{9}$$

M_1 and M_2 are rectangular 3×4 and 4×3 matrices, and $\bar{M}_1$ and $\bar{M}_2$ the transpose of M_1 and M_2, respectively. Similarly N_1 and N_2 are 1×3 and 3×1 rectangular matrices. For brevity we do not write the explicit expressions of any of those matrices. Their calculation is straightforward.

The matrix expressions (8) and (9) for W_{jk} and S_x can now be introduced in Eq. (1). From matrix multiplication rules we get

$$\begin{aligned} -\mathrm{Tr}[H_1', \bar{S}_x]^2 = 2\sum_{j>k} \{ &\textstyle\sum_{n,m} |(E_1M_1 - M_1E_2)_{nm}|^2 \\ &+ \textstyle\sum_{n,m} |(E_2M_2 - M_2E_3)_{nm}|^2 \\ &+ \textstyle\sum_{n,m} |(D_1N_1 - N_1D_2)_{nm}|^2 \\ &+ \textstyle\sum_{n,m} |(D_2N_2 - N_2D_3)_{nm}|^2 \}, \end{aligned}$$

and an expression of the same type for $\mathrm{Tr}\{\bar{S}_x^2\}$. By an expression such as $(E_1M_1 - M_1E_2)_{nm}$ we mean the element at the intersection of the nth row and the mth column of the rectangular matrix $E_1M_1 - M_1E_2$.

The result of the calculation of the traces leads to the following expression:

$$\begin{aligned} S=\tfrac{3}{2}: \quad \langle h^2\Delta\nu^2\rangle_{\mathrm{Av}} = (1/96)g^4\beta^4 \textstyle\sum_j r_{jk}^{-6} [&207(1-3\gamma_{jk}^2)^2 \\ &+ 1512\gamma_{jk}^2(1-\gamma_{jk}^2) + 459(1-\gamma_{jk}^2)^2 \\ &- 108(1-3\gamma_{jk}^2)(\alpha_{jk}^2 - \beta_{jk}^2)]. \end{aligned} \tag{10}$$

It is interesting to compare Eqs. (7) and (10) with the formula (10) of reference 1. For argument's sake we assume a simple cubic lattice with the gradient of the electric field parallel to one of the axes. Then Eqs. (7) and (10) become

$$S=1: \quad \langle h^2\Delta\nu^2\rangle_{\mathrm{Av}} = 28.4 g^4\beta^4 d^{-6},$$

$$S=\tfrac{3}{2}: \quad \langle h^2\Delta\nu^2\rangle_{\mathrm{Av}} = 60.0 g^4\beta^4 d^{-6},$$

where d is the dimension of the unit cell.

Van Vleck's formulas for ordinary magnetic resonance yield:

$$S=1: \quad \langle h^2\Delta\nu^2\rangle_{\mathrm{Av}} = 20.0 g^4\beta^4 d^{-6},$$

$$S=\tfrac{3}{2}: \quad \langle h^2\Delta\nu^2\rangle_{\mathrm{Av}} = 37.4 g^4\beta^4 d^{-6},$$

where we have assumed that the applied static field is parallel to one of the cubic axes.

Case II. Interaction between Resonant and Nonresonant Nuclei Only

The case where resonant nuclei interact with nonresonant nuclei only is much simpler, at least if the gradient of the electric field has the same direction for both types of nuclei, which we shall assume here (except if the nonresonant nuclei have spin $\frac{1}{2}$, when this assumption is unnecessary). For each value of the resonant spin $S=1$ and $S=\frac{3}{2}$, there are three different cases to consider depending on the characteristics of the nonresonant nuclei. These are summarized in Table II.

The interaction Hamiltonian H_1 is written below

with index j for resonant and k' for nonresonant spin.

$$H_1=\sum_{j,k'} W_{jk'}=gg'\beta^2\sum_{jk'} r_{jk'}^{-3}[(1-3\gamma_{jk'}^2)S_{zj}S_{zk'}' -\tfrac{1}{4}(1-3\gamma_{jk'}^2)(S_{+j}S_{-k'}'+S_{-j}S_{+k'}') -\tfrac{3}{2}\gamma_{jk'}(\alpha_{jk'}-i\beta_{jk'})(S_{zj}S_{+k'}'+S_{+j}S_{zk'}') -\tfrac{3}{2}\gamma_{jk'}(\alpha_{jk'}+i\beta_{jk'})(S_{zj}S_{-k'}'+S_{-j}S_{zk'}') -\tfrac{3}{4}(\alpha_{jk'}-i\beta_{jk'})^2S_{+j}S_{+k'}' -\tfrac{3}{4}(\alpha_{jk'}+i\beta_{jk'})^2S_{-j}S_{-k'}'] \quad (11)$$

According to the principles stated in the introduction, the following modification should be made on $W_{jk'}$ and S_x:

(a) Spin operators relative to resonant nuclei:

Cases A_1, A_2, A_3: All operators in Eq. (11) containing $S_{\pm j}$ should be discarded.

Cases B_1, B_2, B_3: $S_{\pm j}$ should be replaced in Eq. (11) by $\bar{S}_{\pm j}$, where $\bar{S}_{\pm j}$ is deduced from $S_{\pm j}$ by equating to zero all the matrix elements except those connecting the states $m=\pm\frac{1}{2}$.

(b) Spin operators relative to nonresonant nuclei:

Cases A_1, B_1: No change.

Cases A_2, B_2: $S_{\pm k'}$ should be replaced by $\bar{S}_{\pm k'}$ which is defined in the same way as $\bar{S}_{\pm j}$.

Cases A_3, B_3: All operators in Eq. (11) containing $S_{\pm k'}$ should be discarded.

(c) Operator $S_x=\sum_j S_{xj}$:

Cases A_1, A_2, A_3: No change.

Cases B_1, B_2, B_3: $\bar{S}_x$ results from S_x by suppression of matrix elements connecting the states $m=\pm\frac{1}{2}$.

After these modifications have been made, Eq. (1) can be used to calculate the second moment of the resonance line.

The results for all cases are summarized compactly in the following formula:

$$\langle h^2\Delta\nu^2\rangle_{\text{Av}}=\tfrac{1}{3}g^2g'^2\beta^4S'(S'+1)\sum_{k'} r_{jk'}^{-6} \times\{(1+F(S)G(S'))(1-3\gamma_{jk'}^2)^2 +9(G(S')+2F(S))\gamma_{jk'}^2(1-\gamma_{jk'}^2) +9F(S)G(S')(1-3\gamma_{jk'}^2)^2\}, \quad (12)$$

where the functions $F(S)$ and $G(S')$ are defined as follows:

$F(1)=0$, $F(\frac{3}{2})=\frac{1}{2}$.

$G(S')=1$ for the cases A_1 and B_1.

$G(S')=\frac{3}{8}(2S'+1)/[S'(S'+1)]$ for the cases A_2 and B_2.

$G(S')=0$ for the cases A_3 and B_3.

These results can again be compared with the straight magnetic resonance case. Let us call

$$a=\sum_{k'} r_{jk'}^{-6}(1-3\gamma_{jk'}^2)^2,$$

$$b=\sum_{k'} r_{jk'}^{-6}\gamma_{jk'}^2(1-\gamma_{jk'}^2),$$

$$c=\sum_{k'} r_{jk'}^{-6}(1-\gamma_{jk'}^2)^2.$$

Van Vleck's formula (28) of reference 1 yields for this case

$$h^2\langle\Delta\nu^2\rangle_{\text{magn}}=\tfrac{1}{3}S'(S'+1)a.$$

For spin 1, Eq. (12) gives for the pure quadrupole resonance line width:

Case A_1: $h^2\langle\Delta\nu^2\rangle_{\text{quadr}}=\frac{1}{3}S'(S'+1)a(1+b/a)$,

Case A_2: $h^2\langle\Delta\nu^2\rangle_{\text{quadr}}=\frac{1}{3}S'(S'+1)a\left\{1+\frac{3}{8}\frac{(2S'+1)}{S'(S'+1)}\frac{b}{a}\right\}$,

Case A_3: $h^2\langle\Delta\nu^2\rangle_{\text{quadr}}=\frac{1}{3}S'(S'+1)a$.

To make the comparison in the spin $\frac{3}{2}$ case we shall assume for simplicity a cubic lattice with the electric field gradient parallel to one of the axes, in which case we have $c=3a+2b$ and

Case B_1: $h^2\langle\Delta\nu^2\rangle_{\text{quadr}}=\frac{1}{3}S'(S'+1)a\{3(1+b/a)\}$,

Case B_2: $h^2\langle\Delta\nu^2\rangle_{\text{quadr}}=\frac{1}{3}S'(S'+1)a \times\left(1+\frac{6}{8}\frac{2S'+1}{S'(S'+1)}\right)\left(1+\frac{b}{a}\right)$,

Case B_3: $h^2\langle\Delta\nu^2\rangle_{\text{quadr}}=\frac{1}{3}S'(S'+1)a\left(1+\frac{b}{a}\right)$.

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