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Line shape analysis in nuclear quadrupole resonance spectroscopy ($I = 3/2$)

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Abstract. Following the treatment of Vega (1973), the theoretical expressions for the second moments in nuclear quadrupole resonance (NQR) due to dipole-dipole interactions have been derived for the system containing the nuclei with spin $I = 3/2$. Cases with the orientation of the static magnetic field and the interactions with the other magnetic nuclei are also dealt with.

Keywords. Nuclear quadrupole resonance; electric field gradient tensor; dipolar interaction; second moment; physical inequivalence; unlike spins.

1. Introduction

The dipole-dipole interaction plays an important role in the majority of nuclear magnetic resonance (NMR) phenomena. Much attention has been paid and useful information is obtained from the line shape analysis in wide line NMR. But very little in nuclear quadrupole resonance (NQR) spectroscopy is found in literature. However the treatment is mainly qualitative, because either the theory, for the most part, is complicated or the phenomena are not sufficiently well studied or understood, to formulate a precise and unified theory. For example, the cases of integer and half integer spins; axially and non-axially symmetric electric field gradient (EFG) tensors; and interactions between equivalent and different nuclei in NQR are to be dealt with separately.

Abragam and Kambe (1953) are the pioneers in deriving expressions in NQR spectroscopy in the cases of axially symmetric field gradients for spins I = 1 and 3/2. Kano (1958) derived expressions for the interactions between physically inequivalent nuclei of spins $I = 3/2$ for polycrystalline samples. Leppelmeier and Hahn (1966) went further to the cases of non-axial symmetry with and without the effects of a magnetic field for $I = 1$ only. Vega (1973) confining to the system with spins $I = 1$, extended the treatment with a different approach to many more cases. The present article gives the follow up of Vega's treatment for a system containing quadurpolar nuclei of spin $I = 3/2$ with an axially symmetric field gradient, including the effects of magnetic field and the interactions between resonant and non-resonant nuclei.

2. Theory of dipolar interactions

The natural width of the quadrupole resonance line, due to a single nucleus in a static electric field, interacting only with the applied rf field would be very sharp. But, in practice, it is not happening because the electric field surrounding the nucleus is subjected to the dynamics and distortions of the crystal lattice. In addition, the nucleus is capable of dipolar interaction with other magnetic nuclei in the crystal, which also causes line broadening. Unlike in the ionic crystals, where the imperfections and impurities in the crystal affect the electric field gradient and line width very much, in covalent crystals, the dipolar interactions are the dominant source for the line width. In this article, we consider the effect of dipolar interactions on the line width, in the absence of the dynamic effects.

We consider a system of interacting nuclei with the hamiltonian (Das and Hahn 1958)

$$\mathcal{H}_T = \mathcal{H}_o + \mathcal{H}_D = \mathcal{H}_Q + \mathcal{H}_Z + \mathcal{H}_D, \tag{1}$$

where
$$\mathcal{H}_Q = \sum_i \mathcal{H}_{Qi} = \sum_i A_i \,(3\, I_{zi}^2 - I_i^2 + \eta_i\,(I_{xi}^2 - I_{yi}^2)), \tag{2}$$

$$\mathcal{H}_Z = \sum_i \mathcal{H}_{Zi} = -\,\hbar\, \underset{\sim}{H} \cdot \sum_i \gamma_i\, \underset{\sim}{I}_i, \tag{3}$$

$$\begin{aligned}\mathcal{H}_D = \sum_{ij} \mathcal{H}_{ij} = \sum_{i>j} \frac{\gamma_i\,\gamma_j\,\hbar^2}{r_{ij}^3}\,[&XOS_{ij}\, I_{xi}\, I_{xj} \\ &+ YOS_{ij}\, I_{yi}\, I_{yj} + ZOS_{ij}\, I_{zi}\, I_{zj} \\ &- 3\, X_{ij}\, Y_{ij}\,(I_{xi}\, I_{yj} + I_{yi}\, I_{xj}) \\ &- 3\, X_{ij}\, Z_{ij}\,(I_{xi}\, I_{zj} + I_{zi}\, I_{xj}) \\ &- 3 Y_{ij}\, Z_{ij}\,(I_{yi}\, I_{zj} + I_{zi}\, I_{yj})],\end{aligned} \tag{4}$$

and
$$A_i = \frac{e^2\, q_i\, Q_i}{4\, I_i\,(2\, I_i - 1)}.$$

Here $\mathcal{H}_o$ is the hamiltonian of the nuclei which includes both the quadrupole interaction $\mathcal{H}_Q$ and interaction with the static field $\mathcal{H}_Z$. $\mathcal{H}_D$ is the dipolar hamiltonian; q and η are the maximum principal field gradient component and the asymmetry parameter of the EFG tensor respectively. $\mathcal{H}$ is the static magnetic field. γ_i, γ_j are the gyromagnetic ratios of the i and j nuclei. I_x, I_y, I_z are the angular momentum operators along the principal field gradient directions. $\underset{\sim}{r}_{ij}$ is the vector joining the i and j nuclei with the direction cosines as X_{ij}, Y_{ij} and Z_{ij} with respect to the principal system. Here we denote that $XOS_{ij} = 1 - 3X_{ij}^2$; $YOS_{ij} = 1 - 3Y_{ij}$ and $ZOS_{ij} = 1 - 3Z_{ij}^2$.

By applying the Van Vleck (1948) method, we get the expression for the second moment of the resonance line as

$$\langle \omega^2 \rangle = \frac{-\,\mathrm{tr}\,[\mathcal{H}_T, I_r]^2}{\hbar^2\,\mathrm{tr}\,[I_r]^2}, \tag{5}$$

where r is the direction of the rf irradiation. In $\mathcal{H}_T$ given by (1), $\mathcal{H}_D$ is split into two parts as $\mathcal{H}_D = \mathcal{H}'_D + \mathcal{H}''_D$ where $\mathcal{H}'_D$ alone commutes with $\mathcal{H}_o$. Only the truncated hamiltonian $\mathcal{H}'_T = \mathcal{H}_o + \mathcal{H}'^{z}_D$ is used in (5), in order to discard the matrix elements which contribute only to the satellite lines. Similarly I_r is also truncated to give only those matrix elements corresponding to the required transition. Then we get the second moment with respect to the central frequency as (Vega 1973)

$$\langle \Delta\,\omega^2 \rangle = \frac{-\,\mathrm{tr}\,[\mathcal{H}'_D, I'_r]^2}{\hbar^2\,\mathrm{tr}\,[I_r]^2}, \tag{6}$$

when we consider the first order truncated hamiltonian $\mathcal{H}'_D$.

To obtain this $\mathcal{H}'_D$, two methods are available in literature (Abragam and Kambe 1953). In the first method, $\mathcal{H}_{ij}$ is modified by introducing suitable projection operators of i and j nuclei. In the second method the matrix elements of $\mathcal{H}_{ij}$ are evaluated and those connecting the off-diagonal elements of different energies are discarded. In the present work, the second method has been used for spin $I = 3/2$, as the first method is impracticable for it (Abragam and Kambe 1953).

3. Second moments for like spins I = 3/2

If N is the number of nuclei in the sample, then the matrices involved in (6) will be in $(2I + 1)^N$ dimensional space. By reducing the dimensionality (Vega 1973), it follows that,

$$\langle \Delta\,\omega^2 \rangle = \frac{-\sum_{i>j} \mathrm{tr}\,[\mathcal{H}'_{ij}, I_{ri} + I_{rj}]^2_{(2I+1)^2}}{n(2I+1)\,\hbar^2\,\mathrm{tr}\,[I_{ri}]^2_{(2I+1)}}, \tag{7}$$

where n is the number of nuclei in the unit cell.

3.1 *Completely equivalent nuclei*

Here we derive expressions for $\langle \Delta\,\omega^2 \rangle$ due to the magnetic dipolar interaction between completely equivalent nuclei having the same magnitude and directions as the EFG tensor.

3.1a $I = 3/2$ $\eta = 0$ $H = 0$: This case is worked out in five steps:
(i) The energies and eigen states of $\mathcal{H}_{oi}$ for the single nucleus with spin $I = 3/2$ are derived from (2) as,

$$E_{\pm 3/2} = 3\mathrm{A} \qquad E_{\pm 1/2} = -3\mathrm{A}, \tag{8a}$$

$$|a\rangle = |3/2\rangle; \ |b\rangle = |-3/2\rangle; |c\rangle = |1/2\rangle \text{ and } |d\rangle = |-1/2\rangle,$$

where $A = e^2 q Q/12$ and transition frequency is $6A/\hbar$.

(ii) The energies and eigenstates of $\mathcal{H}_{oi} + \mathcal{H}_{oj}$ are

$$|aa\rangle, \ |ab\rangle, \ |ba\rangle, \ |bb\rangle, \text{ all having } E = 6A,$$

$$|ac\rangle, |ca\rangle, |ad\rangle, |da\rangle, |bc\rangle, |cb\rangle, |bd\rangle, |db\rangle, \tag{8b}$$

all having $E = 0$ and

$$|cc\rangle, \ |cd\rangle, \ |dc\rangle, \ |dd\rangle \text{ all having } E = -6A,$$

with the understanding that $|mn\rangle = |m\rangle_i |n\rangle_j$. For convenience, these 16 states are numbered as 1, 2, .., 16 in the order given.

(iii) The matrix elements of $\mathcal{H}_{ij}$ are calculated from (4) in the basis set of $\mathcal{H}_{oi}+\mathcal{H}_{oj}$. Then the truncation is done by discarding all the off-diagonal matrix elements, except those connecting the degenerate states of $\mathcal{H}_{oi} + \mathcal{H}_{oj}$.

(iv) The transition $|a\rangle \to |c\rangle$ can be induced by the x and y components of the rf field. Taking the rf irradiation direction along x axis, the symmetric mattrix elements of $(I_{xi} + I_{xj})$ which are responsible for the required transition, are calculated in the basis set of $\mathcal{H}_{oi} + \mathcal{H}_{oj}$ and are given as

$$i_{15} = i_{16} = i_{2\,10} = i_{3\,9} = i_{5\,13} = i_{6\,13} = i_{7\,14} = i_{8\,15} = \sqrt{3}/2. \tag{9}$$

(v) By evaluating the commutators and traces in (7) the expression for the second moment is

$$\langle \Delta \omega^2 \rangle = \frac{\gamma^4 \hbar^2}{16} \sum_{i>j} \frac{1}{r_{ij}^6} [111 + 135\, Z_{ij}^4 - 108\, Z_{ij}^2], \tag{10}$$

for completely equivalent nuclei, in the absence of magnetic field.
3.1b $I = 3/2$ $\eta = 0$ $H \neq 0$: If the magnetic field is applied to the system along any arbitrary direction making an angle θ with the principal z axis, then the degeneracy of the states will be removed. For axially symmetric EFG tensor, there will be zero order mixing of $|1/2\rangle$ and $|-1/2\rangle$ states leading to the new states $|+\rangle$ and $|-\rangle$.

Then the energies and eigenstates of $\mathcal{H}_{0i}$ are (Das and Hahn 1958),

$$E_{\pm 3/2} = 3A \mp \frac{3\xi}{2} \cos\theta, \qquad E_{\pm 1/2} = -3A \mp \frac{f\xi}{2} \cos\theta,$$

$$|a\rangle = |3/2\rangle, \qquad |b\rangle = |-3/2\rangle,$$

$$|c\rangle = |+\rangle = |1/2\rangle \sin\alpha + |-1/2\rangle \cos\alpha,$$

$$|d\rangle = |-\rangle = -|1/2\rangle \cos\alpha + |-1/2\rangle \sin\alpha,$$

with $\xi = \gamma \hbar H_0; \; f = (1 + 4\tan^2\theta)^{1/2}$

and
$$\tan\alpha = \left(\frac{f+1}{f-1}\right)^{1/2}. \tag{11a}$$

Then the states of $\mathcal{H}_{0i} + \mathcal{H}_{0j}$ are given by

$$(|aa\rangle); \; (|ab\rangle, |ba\rangle); \; (|bb\rangle); \; (|ac\rangle, |ca\rangle);$$
$$(|ad\rangle, |da\rangle); (|bc\rangle, |cb\rangle); \; (|bd\rangle, |db\rangle);$$
$$(|cc\rangle); \; (|cd\rangle, |dc\rangle) \text{ and } (|dd\rangle). \tag{11b}$$

The pairs in brackets are degenerate states and a typical state $|mn\rangle$ has the usual understanding as $|m\rangle_i |n\rangle_j$. By numbering these 16 states by 1, 2,. . , 16 in the order given, the non-vanishing elements of the truncated hamiltonian $\mathcal{H}'_{ij}$ in the basis set of $\mathcal{H}_{0i} + \mathcal{H}_{0j}$ are obtained from (4).

For $|a\rangle \rightarrow |c\rangle$ transition, and the rf irradiation direction along x axis, the symmetric matrix elements of $I_{xi} + I_{xj}$ are the same as those given by (9) with the magnitude $(\sqrt{3}/2)\sin\alpha$. By evaluating the traces and commutators in (7) we get,

$$\begin{aligned}
\langle \Delta\omega^2 \rangle = \gamma^4 \hbar^2 \sum_{i>j} \frac{1}{r_{ij}^6} \Big[& 12\, XOS_{ij}^2 \sin^4\alpha \cos^4\alpha \\
& + \frac{3}{8} ZOS_{ij}^2 \Big(\frac{23}{4} + \frac{15}{4}\cos^4\alpha + \frac{9}{2}\cos^2\alpha - \cos^2\alpha \sin^2\alpha \\
& + 2\sin^4\alpha\cos^4\alpha - 3\sin^2\alpha\cos^4\alpha \Big) \\
& + 54\, X_{ij}^2 Z_{ij}^2 (\cos^2\alpha \sin^2\alpha + 2\sin^2\alpha\cos^6\alpha) \\
& + 72\, XOS_{ij} X_{ij} Z_{ij} \sin^3\alpha \cos^5\alpha \\
& + \frac{3}{2} XOS_{ij}\, ZOS_{ij} (\sin^2\alpha\cos^2\alpha - 4\sin^4\alpha\cos^4\alpha + 3\sin^2\alpha\cos^4\alpha) \\
& + X_{ij} Z_{ij}\, ZOS_{ij} (16\sin\alpha\cos\alpha + 18\sin\alpha\cos^3\alpha \\
& + 16\sin\alpha\cos^5\alpha - 18\sin^3\alpha\cos^5\alpha) \Big],
\end{aligned} \tag{12}$$

for the general orientation of the magnetic field. In particular when the magnetic field is along the z-axis (H_z) then (12) becomes

$$\langle \Delta \omega^2 \rangle = \gamma^4 \hbar^2 \sum_{i>j} \frac{1}{r_{ij}^6} \frac{69}{32} ZOS_{ij}^2. \tag{13}$$

Hereafter the magnetic field is considered along z-axis only, as the expressions for $\langle \Delta \omega^2 \rangle$ would be cumbersome.

3.2 *Physically inequivalent nuclei*

Consider two types of physically inequivalent nuclei A and B in the unit cell. Then the second moment becomes

$$\langle \Delta \omega^2 \rangle = \langle \Delta \omega^2 \rangle^{AA} + \langle \Delta \omega^2 \rangle^{BB} + \langle \Delta \omega^2 \rangle^{AB}. \tag{14}$$

Here $\langle \Delta \omega^2 \rangle^{AA}$ and $\langle \Delta \omega^2 \rangle^{BB}$ give the second moments due to the interaction between the nuclei of types A and B respectively. The practical computations of these two terms are treated to be the same as in (7). But in this case the magnitude of I'_r, which depends on the direction of the rf irradiation is different for the two types of nuclei and therefore does not cancel out, whereas it does for completely equivalent nuclei. If α^A is the angle between the rf irradiation direction and the direction for the allowed transition of site A, then,

$$\langle \Delta \omega^2 \rangle^{AA} = \langle \Delta \omega^2 \rangle_{\text{equiv}} \frac{\cos^2 \alpha^A}{\cos^2 \alpha^A + \cos^2 \alpha^B}, \tag{15}$$

where $\langle \Delta \omega^2 \rangle_{\text{equiv}}$ is for completely equivalent nuclei given by (10) and (13). The second term $\langle \Delta \omega^2 \rangle^{AB}$ is given by

$$\langle \Delta \omega^2 \rangle^{AB} = \frac{-\sum_k \operatorname{tr} [\mathcal{H}'_{ik}, (I_{ri} + I_{rk})']^2}{\hbar^2 (2I+1) (\operatorname{tr} [I'_{ri}]^2_{(2I+1)} + \operatorname{tr} [I'_{rk}]^2_{(2I+1)})}, \tag{16}$$

where i, k denote the nuclei of types A and B respectively. Now we rewrite $\mathcal{H}_{ik}$ in such a way that the angular momentum operators which are in the principal co-ordinate systems of the two corresponding nuclei A and B are transformed to only one system. Then we get $I^A_{rk} = \sum_{rr'} R_{rr'} I^B_{r'k}$ where R is the transformation matrix of the co-ordinates (x^A, y^A, z^A) to (x^B, y^B, z^B). The modified hamiltonian $\mathcal{H}_{ik}$ (given as (2·32) by Vega 1973) is used in the calculations.

3.2a $I = 3/2$; $\eta = 0$; $H_z = 0$: The eigen states and energies of $\mathcal{H}_{oi}$ and $(\mathcal{H}_{oi} + \mathcal{H}_{ok})$ are the same as those for completely equivalent nuclei given by (8a) and (8b). The matrix elements of the truncated hamiltonian, thus worked out, are given in the appendix.

For the transition $|a\rangle \to |c\rangle$ with the direction of *rf* irradiation along x axis, the symmetric matrix elements of $(I_{ri} + I_{rk})'$ are calculated from the operator $\cos\alpha^A I^A_{xi} + \cos\alpha^B I^B_{xk}$ and are given as

$$i_{16} = i_{2\,10} = i_{5\,13} = i_{7\,14} = \frac{\sqrt{3}}{2}\cos\alpha^A,$$

$$i_{15} = i_{39} = i_{6\,13} = i_{8\,15} = \frac{\sqrt{3}}{2}\cos\alpha^B. \tag{17}$$

By substituting $h_{\alpha\beta}$, $i_{\alpha\beta}$ in (16), the second movement is obtained as

$$\langle\Delta\omega^2\rangle^{AB} = \frac{\gamma^4\hbar^2}{4}\sum_k \frac{1}{r^6_{ik}}\Big[\frac{80}{9}h^2_{55} + \frac{34}{9}h^2_{56} + \frac{34}{9}h^2_{10\,7} - \frac{9}{8}h_{55}(h_{56}+h_{65})\frac{\cos\alpha^A\cos\alpha^B}{\cos^2\alpha^A+\cos^2\alpha^B} + h^2_{13\,14}\frac{(8\cos^2\alpha^A + 20\cos^2\alpha^B)}{\cos^2\alpha^A+\cos^2\alpha^B} + h^2_{13\,15}\frac{(20\cos^2\alpha^A + 8\cos^2\alpha^B)}{\cos^2\alpha^A+\cos^2\alpha^B}\Big] \tag{18}$$

3.2b $I = 3/2$; $\eta = 0$; $H_z \neq 0$: As the static magnetic field reduces the degeneracy of the states of $(\mathcal{H}_{oi} + \mathcal{H}_{oj})$, the non-vanishing matrix elements of $\mathcal{H}'_{ik}$ are $h_{5\,6}$, $h_{12\,11}$, $h_{14\,15}$ and, all the diagonal elements which are given in the appendix. Then the second moment for $|a\rangle \to |c\rangle$ transition becomes

$$\langle\Delta\omega^2\rangle^{AB} = \frac{\gamma^4\hbar^2}{4}\sum_k \frac{1}{r^6_{ik}}\Big[\frac{80}{9}h^2_{55} + \frac{34}{9}h^2_{56} - \frac{9}{8}(h_{56}+h_{65})h_{55}\frac{\cos\alpha^A\cos\alpha^B}{\cos^2\alpha^A+\cos^2\alpha^B}\Big]. \tag{19}$$

4. Contributions to second moment ($I = 3/2$) for unlike spins

We consider two types of nuclei with spins I and S having different transition frequencies, such that there will be no overlap of quadrupole resonances. Here the matrices involved in (6) will be in $(2I+1)^{N_I}(2S+1)^{N_S}$ dimensional space, where N_I and N_S are the number of nuclei with spins I and S respectively. By reducing the dimensionality, one can write the second moment of I nucleus as

$$\langle\Delta\omega^2\rangle = \langle\Delta\omega^2\rangle^{II} + \langle\Delta\omega^2\rangle^{IS}. \tag{20}$$

where $\langle \Delta\, \omega^2 \rangle^{II}$ is the same as in (7) and $\langle \Delta\, \omega^2 \rangle^{IS}$ is the contribution from dipolar interaction of I nuclei with S nuclei and is given as

$$\langle \Delta\, \omega^2 \rangle^{IS} = \frac{-\sum_{i,s} \mathrm{tr}\, [\mathcal{H}'_{is}, I_{ri}]^2_{(2I+1)\,(2S+1)}}{(2S+1)\, \hbar^2 \sum_i \mathrm{tr}\, [I_{ri}]^2_{(2I+1)\,(2S+1)}}. \tag{21}$$

Now the treatment of I - S interactions of nuclei $S = \frac{1}{2}$, 1, 3/2 is given. Assuming only completely equivalent nuclei in the crystal for $|a\rangle \to |c\rangle$ transition of I nucleus, the results are summarised for different cases.

(i) $I = 3/2 \quad \eta_I = 0 \quad S = \frac{1}{2} \quad H_Z = 0$

$$\langle \Delta\, \omega^2 \rangle^{IS} = 3/2 \quad \gamma_I^2\, \gamma_S^2\, \hbar^2 \sum_{is} \frac{1}{r_{is}^6}. \tag{22}$$

(ii) $I = 3/2 \quad \eta_I = 0 \quad S = \frac{1}{2} \quad H_Z \neq 0$

$$\langle \Delta\, \omega^2 \rangle^{IS} = \tfrac{1}{4}\, \gamma_I^2\, \gamma_S^2\, \hbar^2 \sum_{is} \frac{1}{r_{is}^6} (1 - 3\, Z_{is}^2)^2. \tag{23}$$

(iii) $I = 3/2 \quad \eta_I = 0 \quad S = 1 \quad \eta_S = 0 \quad H_Z = 0$

$$\langle \Delta\, \omega^2 \rangle^{IS} = \tfrac{2}{3}\, \gamma_I^2 \gamma_S^2\, \hbar^2 \sum_{is} \frac{1}{r_{is}^6} (1 + 3\, Z_{is}^2). \tag{24}$$

(iv) $I = 3/2 \quad \eta_I = 0 \quad S = 1 \quad \eta_S \neq 0 \quad H_Z = 0$

$$\langle \Delta\, \omega^2 \rangle^{IS} = 0. \tag{25}$$

(v) $I = 3/2 \quad \eta_I = 0 \quad S = 1 \quad \eta_S = 0 \quad H_Z \neq 0$

$$\langle \Delta\, \omega^2 \rangle^{IS} = \tfrac{2}{3}\, \gamma_I^2 \gamma_S^2\, \hbar^2 \sum_{is} \frac{1}{r_{is}^6} (1 - 3\, Z_{is}^2)^2. \tag{26}$$

(vi) $I = 3/2 \quad \eta_I = 0 \quad S = 1 \quad \eta_S \neq 0 \quad H_Z \neq 0$

$$\langle \Delta\, \omega^2 \rangle^{IS} = 2/3\, \gamma_I^2 \gamma_S^2\, \hbar^2 \sum_{is} \frac{1}{r_{is}^6} \frac{\epsilon^2}{1 + \epsilon^2} ZOS_{is}^2. \tag{27}$$

with $\epsilon = \dfrac{2\,\gamma_s\,\hbar\,H_z}{A_s\,\eta_s}.$

(vii) $I = 3/2 \quad \eta_I = 0 \quad S = 3/2 \quad \eta_S = 0 \quad H_Z = 0$

$$\langle \Delta\,\omega^2 \rangle^{IS} = \tfrac{1}{4}\,\gamma_I^2\,\gamma_S^2\,\hbar^2 \sum_{is} \frac{1}{r_{is}^6}\,(15 + 9\,Z_{is}^2). \tag{28}$$

(viii) $I = 3/2 \quad \eta_I = 0 \quad S = 3/2 \quad \eta_S = 0 \quad H_Z \neq 0$

$$\langle \Delta\,\omega^2 \rangle^{IS} = \tfrac{5}{4}\,\gamma_I^2\,\gamma_S^2\,\hbar^2 \sum_{is} \frac{1}{r_{is}^6}(1 - 3Z_{is})^2. \tag{29}$$

(ix) $I = 3/2 \quad \eta_I = 0 \quad S = 3/2 \quad \eta_S \neq 0 \quad H_Z = 0$

$$\langle \Delta\,\omega^2 \rangle^{IS} = \tfrac{1}{4}\,\gamma_I^2\,\gamma_S^3\,\hbar^2 \sum_{is} \frac{1}{r_{is}^6}\,\frac{1}{(\eta_S^2 + 3)}\,[(21\,\eta_S^2 + 45)$$

$$+ Z_{is}^2\,(27 - 9\,\eta_S^2) - 18\,\eta_S\,(X_{is}^2 - Y_{is}^2)]. \tag{30}$$

5. Discussion

Expressions to various contributions and the formulae for the second moments derived in this paper are compact and relatively simple for computations unlike the formula given by Grigolini (1972) for arbitrary spins and arbitrary directions of the magnetic field. The equations (22), (24) and (28) agree well with those derived by Abragam and Kambe (1953). In the case of completely equivalent nuclei, the derived expression (10) differs from that of Abragam and Kambe's (1953) by a missing term $3/8\ ZOS_{ij}\ (XOS_{ij} - YOS_{ij})$. The essential difference between the present method and their method lies in the choice of the basis states. We had taken a general basis state $|m_i, m_j\rangle$, whereas even and odd basis states namely $(|m_i\,m_j\rangle \pm |m_j\ m_i\rangle)/\sqrt{2}$ are chosen by Abragam and Kambe (1953). In the case of completely equivalent nuclei and in the presence of the magnetic field along z axis, (14) is worked out for the two choices of the basis states and comes out to be the same. Thus the difference in (10) may be due to computational error.

Ambrosetti *et al* (1973) worked out the second moment numerically for ^{14}N resonance in N–N' — dideuterated para chloroaniline for different orientations of the magnetic field using the Grigolini (1972) method. Vega (1973) had tested his formulae to ^{14}N resonance in para-chloroaniline. Kano (1958) compared the theoretical line widths in powder samples of $NaClO_3$ and $NaBrO_3$ with the experimentally observed line widths (Koi 1957; Fuke and Koi 1958) in crystals.

Results of the present work are applied to sodium chlorate crystal and are presented as a separate paper.

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Appendix

The non-vanishing matrix elements of $\mathcal{H}_{ij}$ for physically inequivalent nuclei $I = 3/2$ without magnetic field:

$$h_{11} = (9/4)\,(R_{zz}\,ZOS_{ik} - 3\,R_{yz}\,Y_{ik}\,Z_{ik} - 3R_{xz}\,X_{ik}\,Z_{ik}),$$

with $h_{11} = -\,h_{22} = -\,h_{33} = h_{44}$;

$$h_{55} = (3/4)\,(R_{zz}\,ZOS_{ik} - 3R_{yz}\,Y_{ik}\,Z_{ik} - 3R_{xz}\,X_{ik}\,Z_{ik}),$$

with $h_{55} = h_{66} = -\,h_{77} - h_{88} = -\,h_{99} = -\,h_{10\ 10}$;

$$h_{13\ 13} = \tfrac{1}{4}\,(R_{zz}\,ZOS_{ik} - 3R_{yz}\,Y_{ik}\,Z_{ik} - 3R_{xz}\,X_{ik}\,Z_{ik}),$$

with $h_{13\ 13} = -\,h_{14\ 14} = -\,h_{15\ 15} = h_{16\ 16} = \tfrac{1}{3}\,h_{11\ \ 11} = \tfrac{1}{3}\,h_{12\ 12}$;

$$h_{56} = (3/4)\,(R_{xx}\,XOS_{ik} - 3\,R_{yx}\,X_{ik}\,Y_{ik} - 3R_{zx}\,X_{ik}\,Z_{ik})$$
$$+ (3/4)\,(R_{yy}\,YOS_{ik} - 3R_{xy}\,X_{ik}\,Y_{ik} - 3R_{zy}\,Y_{ik}\,Z_{ik})$$
$$- (3/4)\,i\,R_{xy}\,XOS_{ik} - 3R_{yy}\,X_{ik}\,Y_{ik} - 3R_{zy}\,X_{ik}\,Z_{ik})$$
$$+ (3/4)\,i\,R_{yx}\,YOS_{ik} - 3R_{xx}\,X_{ik}\,Y_{ik} - 3R_{zk}\,Y_{ik}\,Z_{ik}),$$

with $h_{56} = h_{12\ 11} = 3/4\ h_{14\ 15}$;

$$h_{57} = (3/2)\,(R_{zx}\,ZOS_{ik} - 3R_{xx}\,X_{ik}\,Z_{ik} - 3R_{yx}\,Y_{ik}\,Z_{ik})$$
$$+ (3/2)\,i\,(R_{zy}\,ZOS_{ik} - 3R_{yy}\,Y_{ik}\,Z_{ik} - 3R_{xy}\,X_{ik}\,Z_{ik}),$$

with $h_{57} = -\,h_{9\ 11} = 3h_{13\ 14} = -\,3h_{15\ 16}$;

$$h_{7\ 10} = (3/4)\,(R_{xx}\,XOS_{ik} - 3R_{yx}\,X_{ik}\,Y_{ik} - 3R_{zx}\,X_{ik}\,Z_{ik})$$
$$- (3/4)\,(R_{yy}\,YOS_{ik} - 3R_{xy}\,X_{ik}\,Y_{ik} - 3R_{zy}\,Y_{ik}\,Z_{ik})$$
$$+ (3/4)\,i\,(R_{xy}\,XOS_{ik} - 3R_{yy}\,X_{ik}\,Y_{ik} - 3R_{zy}\,X_{ik}\,Z_{ik})$$
$$+ (3/4)\,i\,(R_{yx}\,YOS_{ik} - 3R_{xx}\,X_{ik}\,Y_{ik} - 3R_{zx}\,Y_{ik}\,Z_{ik}),$$

with $h_{7\ 10} = h_{89} = 3/4\ h_{13\ 16}$;

$$h_{68} = (3/2)\,(R_{xz}\, XOS_{ik} - 3R_{zz}\, X_{ik}\, Z_{ik} - 3R_{yz}\, X_{ik}\, Y_{ik})$$
$$+ (3/2)\, i\,(R_{yz}\, YOS_{ik} - 3R_{zz}\, Y_{ik}\, Z_{ik} - 3R_{xz}\, X_{ik}\, Y_{ik}),$$

with $h_{68} = -h_{10\,12} = 3h_{13\,15} = -h_{14\,16}$.

Here $h_{\alpha\beta} = h^{*}_{\beta\alpha}$.

All the elements are in the units of $\gamma^2\hbar^2/r^3_{ik}$.

i, other than in the place of suffix denotes the imaginary number $\sqrt{-1}$.

List of symbols

$\mathcal{H}_T$	total hamiltonian
$\mathcal{H}_o$	the sum of pure and zeeman quadrupole hamiltonians
$\mathcal{H}_D$	the dipolar hamiltonian
$\mathcal{H}'_D$	the truncated dipolar hamiltonian which commutes with $\mathcal{H}_o$
$\mathcal{H}''_D$	the part of $\mathcal{H}_D$ which does not commute with $\mathcal{H}_o$
$\mathcal{H}_{oi}$	the hamiltonian $\mathcal{H}_o$ for single ith nucleus
$\mathcal{H}_{ij}$	the dipolar hamiltonian between i and j nuclei
$\mathcal{H}_{oi} + \mathcal{H}_{oj}$	the hamiltonian for i and j nuclei combined system
η	the asymmetry parameter
$\langle\Delta\omega^2\rangle$	the second moment with respect to the central frequency.
ω	the frequency
H	the static magnetic field
H_z	the static magnetic field along z axis
xyz	the principal field gradient system
γ	the gyromagnetic ratio
$\underset{\sim}{r}_{ij}$	the position vector between i and j nuclei
r in I_r	is the direction of rf irradiation
I	the spin of the nucleus
N	the number of nuclei in the sample
n	the number of nuclei in the unit cell

X_{ij}, Y_{ij} and Z_{ij} are the direction cosines of $\mathbf{r}_{ij}$ vector.

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