A Spherical Tensor Method for Pure NQR *

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The multipole operator technique is used to exploit the rotational invariance of the Hamiltonian. The technique and its effectiveness for the pure quadrupole hamiltonian with arbitrary asymmetry parameter are discussed for spins $\leqq 5/2$. The time evolution of the quadrupolar alignment tensor is presented analytically for various spins. The dynamics of the full density matrix are given.

Introduction

The applications of spherical tensor techniques to magnetic resonance problems have been well-documented. In this paper, we examine the consequences of one such technique [1] to pure NQR spectra. We discuss the eigenvalue problem of NQR from a frequency viewpoint. Secular equations in frequencies of spin 1, 3/2, and 5/2 are obtained and solved in terms of the nuclear electric quadrupole coupling constant and the asymmetry parameter η. This "direct" method as opposed to the "indirect" method of computing the energy eigenvalues with state-basis wavefunctions was first stressed by Banwell and Primas [2]. The solutions agree exactly with the results obtainable either analytically or numerically from energy eigenvalue problems. Exact solutions to the energy eigenvalues have been given earlier by several authors, and by Creel et al. in a recent series of papers [3–5].

In addition to the above, our objective is to present solutions for the NQR signal measured after a pulse or series of pulses. The relaxation processes due to lattice-quadrupole interactions will be considered later.

A set of irreducible tensor operators denoted by $Y^{(k)q}(I)$ where k refers to the tensor rank and q the spherical component have been defined elsewhere [6]. We refer to the relevant properties here.

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General Formalism

1) Unitarity

$$Y^{(k)q}(I) = (i)^k \sqrt{(2k+1)(2I+1)} \cdot \sum_{MM'} (-1)^{I-M} \begin{pmatrix} I & k & I \\ -M & q & M' \end{pmatrix} |IM\rangle\langle IM'| . \quad (1)$$

2) Adjoint

$$[Y^{(k)q}(I)]^{+} = (-1)^{k-q}\, Y^{(k)-q}(I) = Y_q^{(k)}(I) . \quad (2)$$

3) Orthonormality

$$\langle\langle Y^{(k)q}(I) \mid Y^{(k')q'}(I)\rangle\rangle = \mathrm{tr}\,\{(Y^{(k)q}(I))^{+}\, Y^{(k')q'}(I)\} = \delta_{kk'}\delta_{qq'}(2I+1) . \quad (3)$$

For each spin I, the set contains $(2I+1)^2$ operators and k varies from 0 to $2I$, q from $-k$ to k. The observables associated with each $Y^{(k)q}(I)$ will be denoted as $\Phi^{(k)q}$.

Thus the density operator can be expressed in this operator basis set as

$$\sigma = \frac{1}{(2I+1)} \sum_{k=0}^{2I} \sum_{q=-k}^{k} Y^{(k)q}(I)\, \Phi_q^{(k)} . \quad (4)$$

The pure quadrupole Hamiltonian in the principal axis frame can be written as

$$\mathscr{H}_{\mathrm{asymm}} = \frac{e^2 Q q}{4I(2I-1)} \left[(3 I_z^2 - I^2) + \frac{\eta}{2}(I_+^2 + I_-^2) \right] . \quad (5)$$

$e^2 Q q$ being the nuclear electric quadrupole coupling constant and η the asymmetry parameter. We can rewrite this in the operator basis using a set of relations presented in Table 1 of [6].

$$\mathscr{H}_{\text{asymm}} = -\frac{e^2 Q q}{4}\sqrt{\frac{(2I+3)(I+1)}{5I(2I-1)}}\left\{Y^{(2)0}(I) + \frac{\eta}{\sqrt{6}}\left(Y^{(2)2}(I) + Y^{(2)-2}(I)\right)\right\}. \tag{6}$$

The Liouville equation,

$$i\hbar\frac{\partial\sigma}{\partial t}[\mathscr{H}, \sigma] \tag{7}$$

can then be expressed as

$$i\hbar\left\langle\!\!\left\langle Y^{(k')q'}(I) \,\Big|\, \sum_{k,q} Y^{(k)q}(I)\frac{\partial\Phi_q^{(k)}}{\partial t}\right\rangle\!\!\right\rangle = -A\left\{\left\langle\!\!\left\langle Y^{(k')q'}(I) \,|\, [Y^{(2)0}(I), \sum_{kq} Y^{(k)q}(I)\,\Phi_q^{(k)}]\right.\right.\right.$$
$$\left.\left. - \frac{\eta}{\sqrt{6}}\sum_{q=-2,2}\left\langle\!\!\left\langle Y^{(k')q'}(I)\,|\,[Y^{(2)q}(I), \sum_{kq} Y^{(k)q}(I)\,\Phi_q^{(k)}]\right\rangle\!\!\right\rangle\right\}\right.$$

where

$$A = \frac{e^2 Qq}{4}\sqrt{\frac{(2I+3)(I+1)}{5I(2I-1)}}\,. \tag{8}$$

The general commutation relation $[Y^{(l)m}(I), Y^{(k)q}(I)]$ have also been given in [6], and we make use of the Wigner $3-j$ symbols to arrive at the following differential equation for $\Phi_q^{(k)}(t)$.

$$\begin{aligned}
\hbar\frac{\partial}{\partial t}\Phi_q^{(k)} = {} & \frac{3}{2}\bar{Q}\,q\sqrt{\frac{(2I+k+2)(2I-k)[(k+1)^2-q^2]}{I^2(2I-1)^2(2k+1)(2k+3)}}\;\Phi_q^{(k-1)} \\
& - \frac{3}{2}\bar{Q}\,q\sqrt{\frac{(k^2-q^2)(2I+k+1)(2I-k+1)}{I^2(2I-1)^2(2k+1)(2k-1)}}\;\Phi_q^{(k-1)} \\
& + \frac{\bar{Q}}{4}\eta\sqrt{\frac{(k-q+1)(k-q+2)(k-q+3)(k+q)(2I+k+2)(2I-k)}{(2k+3)(2k+1)I^2(2I-1)^2}}\;\Phi_{q-2}^{(k\mp1)} \\
& + \frac{\bar{Q}}{4}\eta\sqrt{\frac{(k+q-2)(k+q-1)(k+q)(k-q+1)(2I+k+1)(2I-k+1)}{I^2(2I-1)^2(2k+1)(2k-1)}}\;\Phi_{q-2}^{(k\mp1)} \\
& - \frac{\bar{Q}}{4}\eta\sqrt{\frac{(k+q+1)(k+q+2)(k+q+3)(k-q)(2I+k+2)(2I-k)}{I^2(2I-1)^2(2k+1)(2k+3)}}\;\Phi_{q+2}^{(k\mp1)} \\
& - \frac{\bar{Q}}{4}\eta\sqrt{\frac{(k-q-2)(k-q-1)(k-q)(k+q+1)(2I+k+1)(2I-k+1)}{I^2(2I-1)^2(2k+1)(2k-1)}}\;\Phi_{q+2}^{(k\mp1)}\,.
\end{aligned} \tag{9}$$

where $\bar{Q} = \frac{1}{2}e^2 Q\,q$. When $\eta = 0$, this reduces to (13) of [6].

This is a system of coupled differential equations of first order of dimension $(2I+1)^2$ with constant coefficients. A closer look suggests that this equation can be rewritten as

$$\frac{\partial}{\partial t}\Phi_q^{(k)} = \sum_{q'=q,\,q\pm2}{}' \{C_{q'}\,\Phi_{q'}^{(k+1)} + D_{q'}\,\Phi_{q'}^{(k-1)}\} \tag{10}$$

where C's and D's are the appropriate square root factors of the previous equation. Thus, the differential equation displays a tridiagonal feature.

$$\frac{\partial}{\partial t}\begin{pmatrix}|\Phi_q^{(1)}|\\ |\Phi_q^{(2)}|\\ |\Phi_q^{(3)}|\\ \vdots\end{pmatrix} = i\begin{pmatrix}0 & A & 0 & \cdots & \cdots & \\ A^+ & 0 & B & 0 & \cdots & \\ 0 & B^+ & 0 & C & 0 & \cdots\\ \vdots & \vdots & \vdots & & & \end{pmatrix}\begin{pmatrix}|\Phi_q^{(1)}|\\ |\Phi_q^{(2)}|\\ |\Phi_q^{(3)}|\\ \vdots\end{pmatrix}. \tag{11}$$

The system also blocks out into two submatrices, one corresponding to odd q and the other to even q. A, B, C etc. are coefficient matrices obtained by substituting the appropriate k and q values. The maximum k for each spin is $k = 2I$. We shall discuss the case of individual spins below.

Spin 1

The conventional picture leads to three energy levels in the presence of asymmetry, namely $|0\rangle$, $|1\rangle$, $|-1\rangle$. There are two single quantum ($\Delta m = \pm 1$) and one double quantum ($\Delta m = \pm 2$) frequency. These are $\frac{3e^2Qq}{4\hbar}(1 \pm \eta/3)$ and $\frac{e^2Qq}{2\hbar}\eta$ respectively. In the frequency picture, a three-level system has nine frequencies, three of which are of zero quanta (populations), four are single quanta (two upward and two downward) and two are double quanta. These are illustrated in Figure 1. The nine frequencies are the eigenvalues of the Liouvillian matrix derived from (9) with $I = 1$.

In our notation $\Phi_0^{(2)}$ is a constant and $\Phi_0^{(0)}$ is identity. Then the differential (9) leads to two blocks of matrices, a 4×4 matrix for odd q and a 3×3 matrix for even q. These contain the single and double quantum frequencies respectively. They are given below for

odd q

$$\frac{\partial}{\partial t}\begin{pmatrix}\Phi_1^{(1)}\\ \Phi_{-1}^{(1)}\\ \hline \Phi_1^{(2)}\\ \Phi_{-1}^{(2)}\end{pmatrix} = \frac{\bar{Q}}{2\hbar}\left(\begin{array}{cc|cc} 0 & 0 & 3 & +\eta\\ 0 & 0 & -\eta & -3\\ \hline -3 & +\eta & 0 & 0\\ -\eta & 3 & 0 & 0\end{array}\right)\begin{pmatrix}\Phi_1^{(1)}\\ \Phi_{-1}^{(1)}\\ \hline \Phi_1^{(2)}\\ \Phi_{-1}^{(2)}\end{pmatrix} \tag{12}$$

with eigenvalues $\pm i\frac{3e^2Qq}{4\hbar}(1 \pm \eta/3)$

and even q

$$\frac{\partial}{\partial t}\begin{pmatrix}\Phi_0^{(1)}\\ \Phi_2^{(2)}\\ \Phi_{-2}^{(2)}\end{pmatrix} = \frac{-\bar{Q}\eta}{\sqrt{2}\hbar}\begin{pmatrix} 0 & 1 & -1\\ -1 & 0 & 0\\ 1 & 0 & 0\end{pmatrix}\begin{pmatrix}\Phi_0^{(1)}\\ \Phi_2^{(2)}\\ \Phi_{-2}^{(2)}\end{pmatrix} \tag{13}$$

with eigenvalues $0, \pm i\frac{e^2Qq}{2\hbar}\eta$.

The complete solution to the density matrix in this case can be easily computed from arbitrary initial polarisations $\Phi_q^{(k)}(0)$. They are given in Table 1.

Spin 3/2

In this case, we have only two levels, each of which is doubly degenerate even in the presence of asymmetry and are designated by $|\pm 3/2\rangle$ and $|\pm 1/2\rangle$. The frequency spectrum of a four-level system contains 16 frequencies and can be decomposed into four zero quanta, six single quanta, four double quanta and two triple quanta. The differential equation (9) enables the system to be split up into one 8×8 matrix for odd q and one 7×7 matrix for even q, $\Phi_0^{(0)}$ being identity. The matrix for odd q is given below

$$\frac{\partial}{\partial t}\begin{pmatrix}\Phi_1^{(1)}\\ \Phi_{-1}^{(1)}\\ \hline \Phi_1^{(2)}\\ \Phi_{-1}^{(2)}\\ \hline \Phi_3^{(3)}\\ \Phi_1^{(3)}\\ \Phi_{-1}^{(3)}\\ \Phi_{-3}^{(3)}\end{pmatrix} = \frac{\bar{Q}}{\hbar}\left(\begin{array}{cc|cc|cccc}
0 & 0 & \sqrt{\frac{3}{5}} & \frac{\eta}{\sqrt{15}} & 0 & 0 & 0 & 0\\
0 & 0 & -\frac{\eta}{\sqrt{15}} & -\sqrt{\frac{3}{5}} & 0 & 0 & 0 & 0\\ \hline
-\sqrt{\frac{3}{5}} & \frac{\eta}{\sqrt{15}} & 0 & 0 & -\frac{\eta}{\sqrt{6}} & \sqrt{\frac{2}{5}} & \frac{\eta}{\sqrt{10}} & 0\\
-\frac{\eta}{\sqrt{15}} & \sqrt{\frac{3}{5}} & 0 & 0 & 0 & -\frac{\eta}{\sqrt{10}} & -\sqrt{\frac{2}{5}} & \frac{\eta}{\sqrt{6}}\\ \hline
0 & 0 & \frac{\eta}{\sqrt{6}} & 0 & 0 & 0 & 0 & 0\\
0 & 0 & -\sqrt{\frac{2}{5}} & \frac{\eta}{\sqrt{10}} & 0 & 0 & 0 & 0\\
0 & 0 & -\frac{\eta}{\sqrt{10}} & \sqrt{\frac{2}{5}} & 0 & 0 & 0 & 0\\
0 & 0 & 0 & -\frac{\eta}{\sqrt{6}} & 0 & 0 & 0 & 0
\end{array}\right)\begin{pmatrix}\Phi_1^{(1)}\\ \Phi_{-1}^{(1)}\\ \hline \Phi_1^{(2)}\\ \Phi_{-1}^{(2)}\\ \hline \Phi_3^{(3)}\\ \Phi_1^{(3)}\\ \Phi_{-1}^{(3)}\\ \Phi_{-3}^{(3)}\end{pmatrix}. \tag{14}$$

Table 1. Evolution of polarisations $\Phi_q^{(k)}(t)$ as a function of $\Phi_q^{(k)}(0)$ for spin 1.

$$\begin{pmatrix} \Phi_1^{(1)}(t) \\ \Phi_1^{(2)}(t) \\ \Phi_{-1}^{(1)}(t) \\ \Phi_{-1}^{(2)}(t) \end{pmatrix} = \frac{1}{2} \begin{pmatrix} \cos A + \cos B & \sin A - \sin B & \cos B - \cos A & \sin B + \sin A \\ \sin B - \sin A & \cos A + \cos B & \sin A + \sin B & \cos A - \cos B \\ \cos B - \cos A & \sin A - \sin B & \cos A + \cos B & \sin B - \sin A \\ -\sin A - \sin B & \cos A - \cos B & \sin A - \sin B & \cos A + \cos B \end{pmatrix} \begin{pmatrix} \Phi_1^{(1)}(0) \\ \Phi_1^{(2)}(0) \\ \Phi_{-1}^{(1)}(0) \\ \Phi_{-1}^{(2)}(0) \end{pmatrix}$$

$$A = \frac{(\eta+3)\,\tilde{Q}\,t}{2}; \qquad B = \frac{(\eta-3)\,\tilde{Q}\,t}{2}$$

$$\begin{pmatrix} \Phi_2^{(2)}(t) \\ \Phi_{-2}^{(2)}(t) \\ \Phi_0^{(1)}(t) \end{pmatrix} = \frac{1}{2} \begin{pmatrix} 1 + \cos \tilde{Q}\,\eta\,t & 1 - \cos \tilde{Q}\,\eta\,t & \sqrt{2} \sin \tilde{Q}\,t\,\eta \\ 1 - \cos \tilde{Q}\,\eta\,t & 1 + \cos \tilde{Q}\,\eta\,t & -\sqrt{2} \sin \tilde{Q}\,\eta\,t \\ -\sqrt{2} \sin \tilde{Q}\,\eta\,t & \sqrt{2} \sin \tilde{Q}\,\eta\,t & \cos \tilde{Q}\,\eta\,t \end{pmatrix} \begin{pmatrix} \Phi_2^{(2)}(0) \\ \Phi_{-2}^{(2)}(0) \\ \Phi_0^{1}(0) \end{pmatrix}$$

If we denote the blocks of (14) by

$$i \begin{pmatrix} 0 & A & 0 \\ A^+ & 0 & B \\ 0 & B^+ & 0 \end{pmatrix} \tag{15}$$

elementary matrix algebra leads to

$$\det |\lambda^2 - A^+ A - B B^+| = 0$$

as the secular equation for the matrix, which for the present case is $(\lambda^2 + 1 + \eta^2/3)^2 = 0$, λ being the eigenvalue. The eigenvalue are thus

$$\left(0, 0, 0, 0, \pm i \frac{e^2 Q q}{2\hbar} \sqrt{(1+\eta^2/3)}\,, \pm i \frac{e^2 Q q}{2\hbar} \sqrt{(1+\eta^2/3)}\right).$$

Exactly the same information is contained in the 7×7 matrix for even q, given below.

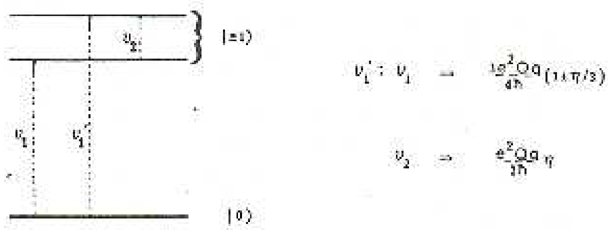

Fig. 1. Frequency spectrum of spin 1.

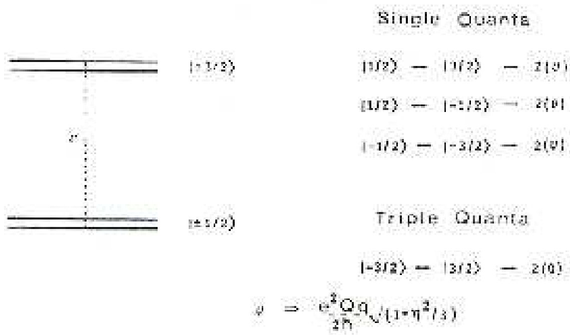

Fig. 2. Frequency spectrum of spin 3/2.

$$\frac{\partial}{\partial t} \begin{pmatrix} \Phi_0^{(1)} \\ \hline \Phi_2^{(2)} \\ \Phi_0^{(2)} \\ \Phi_{-2}^{(2)} \\ \hline \Phi_2^{(3)} \\ \Phi_0^{(3)} \\ \Phi_{-2}^{(3)} \end{pmatrix} = \frac{\tilde{Q}}{\hbar} \left(\begin{array}{c|ccc|ccc} 0 & -\sqrt{\frac{2}{15}}\,\eta & 0 & \sqrt{\frac{2}{15}}\,\eta & 0 & 0 & 0 \\ \hline \sqrt{\frac{2}{15}}\,\eta & 0 & 0 & 0 & 1 & \frac{\eta}{\sqrt{30}} & 0 \\ 0 & 0 & 0 & 0 & -\frac{\eta}{\sqrt{6}} & 0 & \frac{\eta}{\sqrt{6}} \\ -\sqrt{\frac{2}{15}}\,\eta & 0 & 0 & 0 & 0 & -\frac{\eta}{\sqrt{30}} & -1 \\ \hline 0 & -1 & \frac{\eta}{\sqrt{6}} & 0 & 0 & 0 & 0 \\ 0 & -\frac{\eta}{\sqrt{30}} & 0 & \frac{\eta}{\sqrt{30}} & 0 & 0 & 0 \\ 0 & 0 & -\frac{\eta}{\sqrt{6}} & 1 & 0 & 0 & 0 \end{array}\right) \begin{pmatrix} \Phi_0^{(1)} \\ \hline \Phi_2^{(2)} \\ \Phi_0^{(2)} \\ \Phi_{-2}^{(2)} \\ \hline \Phi_2^{(3)} \\ \Phi_0^{(3)} \\ \Phi_{-2}^{(3)} \end{pmatrix} \tag{16}$$

$$
\frac{\partial}{\partial t}
\begin{pmatrix}
\Phi^{(1)}_{1}\\ \Phi^{(1)}_{-1}\\ \Phi^{(2)}_{1}\\ \Phi^{(2)}_{-1}\\ \Phi^{(3)}_{3}\\ \Phi^{(3)}_{1}\\ \Phi^{(3)}_{-1}\\ \Phi^{(3)}_{-3}\\ \Phi^{(4)}_{3}\\ \Phi^{(4)}_{1}\\ \Phi^{(4)}_{-1}\\ \Phi^{(4)}_{-3}\\ \Phi^{(5)}_{5}\\ \Phi^{(5)}_{3}\\ \Phi^{(5)}_{1}\\ \Phi^{(5)}_{-1}\\ \Phi^{(5)}_{-3}\\ \Phi^{(5)}_{-5}
\end{pmatrix}
=\frac{\tilde{Q}}{\hbar}
\left(\begin{array}{cc|cc|cccc|cccc|cccccc}
0 & 0 & \frac{3\sqrt{2}}{5\sqrt{5}} & \frac{-\eta\sqrt{2}}{5\sqrt{5}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0\\
0 & 0 & \frac{\eta\sqrt{2}}{5\sqrt{5}} & \frac{-3\sqrt{2}}{5\sqrt{5}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0\\
\hline
\frac{-3\sqrt{2}}{5\sqrt{5}} & \frac{-\eta\sqrt{2}}{5\sqrt{5}} & 0 & 0 & \frac{9\eta}{10\sqrt{14}} & \frac{9\sqrt{3}}{5\sqrt{70}} & \frac{-9\eta\sqrt{3}}{10\sqrt{70}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0\\
\frac{\eta\sqrt{2}}{5\sqrt{5}} & \frac{3\sqrt{2}}{5\sqrt{5}} & 0 & 0 & 0 & \frac{9\eta\sqrt{3}}{10\sqrt{70}} & \frac{-9\sqrt{3}}{5\sqrt{70}} & \frac{-9\eta}{10\sqrt{14}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0\\
\hline
0 & 0 & \frac{-9\eta}{10\sqrt{14}} & 0 & 0 & 0 & 0 & 0 & \frac{3}{2\sqrt{5}} & \frac{-\eta}{2\sqrt{35}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0\\
0 & 0 & \frac{-9\sqrt{3}}{5\sqrt{70}} & \frac{-9\eta\sqrt{3}}{10\sqrt{70}} & 0 & 0 & 0 & 0 & \frac{\eta}{2\sqrt{3}} & \frac{\sqrt{3}}{2\sqrt{7}} & \frac{-\eta}{\sqrt{21}} & 0 & 0 & 0 & 0 & 0 & 0 & 0\\
0 & 0 & \frac{9\eta\sqrt{3}}{10\sqrt{70}} & \frac{9\sqrt{3}}{5\sqrt{70}} & 0 & 0 & 0 & 0 & 0 & \frac{\eta}{\sqrt{21}} & \frac{-\sqrt{3}}{2\sqrt{7}} & \frac{-\eta}{2\sqrt{3}} & 0 & 0 & 0 & 0 & 0 & 0\\
0 & 0 & 0 & \frac{9\eta}{10\sqrt{14}} & 0 & 0 & 0 & 0 & 0 & 0 & \frac{\eta}{2\sqrt{35}} & \frac{-3}{2\sqrt{5}} & 0 & 0 & 0 & 0 & 0 & 0\\
\hline
0 & 0 & 0 & 0 & \frac{-3}{2\sqrt{5}} & \frac{-\eta}{2\sqrt{3}} & 0 & 0 & 0 & 0 & 0 & 0 & \frac{\eta}{2\sqrt{5}} & \frac{3}{5} & \frac{-\eta\sqrt{7}}{10\sqrt{6}} & 0 & 0 & 0\\
0 & 0 & 0 & 0 & \frac{\eta}{2\sqrt{35}} & \frac{-\sqrt{3}}{2\sqrt{7}} & \frac{-\eta}{\sqrt{21}} & 0 & 0 & 0 & 0 & 0 & 0 & \frac{\eta\sqrt{7}}{10} & \frac{\sqrt{3}}{5\sqrt{2}} & \frac{-\eta}{2\sqrt{6}} & 0 & 0\\
0 & 0 & 0 & 0 & 0 & \frac{\eta}{\sqrt{21}} & \frac{\sqrt{3}}{2\sqrt{7}} & \frac{-\eta}{2\sqrt{35}} & 0 & 0 & 0 & 0 & 0 & 0 & \frac{\eta}{2\sqrt{6}} & \frac{-\sqrt{3}}{5\sqrt{2}} & \frac{-\eta\sqrt{7}}{10} & 0\\
0 & 0 & 0 & 0 & 0 & 0 & \frac{\eta}{2\sqrt{3}} & \frac{3}{2\sqrt{5}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{\eta\sqrt{7}}{10\sqrt{6}} & \frac{-3}{5} & \frac{-\eta}{2\sqrt{5}}\\
\hline
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{-\eta}{2\sqrt{5}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0\\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{-3}{5} & \frac{-\eta\sqrt{7}}{10} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0\\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{\eta\sqrt{7}}{10\sqrt{6}} & \frac{-\sqrt{3}}{5\sqrt{2}} & \frac{-\eta}{2\sqrt{6}} & 0 & 0 & 0 & 0 & 0 & 0 & 0\\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{\eta}{2\sqrt{6}} & \frac{\sqrt{3}}{5\sqrt{2}} & \frac{-\eta\sqrt{7}}{10\sqrt{6}} & 0 & 0 & 0 & 0 & 0 & 0\\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{\eta\sqrt{7}}{10} & \frac{3}{5} & 0 & 0 & 0 & 0 & 0 & 0\\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{\eta}{2\sqrt{5}} & 0 & 0 & 0 & 0 & 0 & 0
\end{array}\right)
\begin{pmatrix}
\Phi^{(1)}_{1}\\ \Phi^{(1)}_{-1}\\ \Phi^{(2)}_{1}\\ \Phi^{(2)}_{-1}\\ \Phi^{(3)}_{3}\\ \Phi^{(3)}_{1}\\ \Phi^{(3)}_{-1}\\ \Phi^{(3)}_{-3}\\ \Phi^{(4)}_{3}\\ \Phi^{(4)}_{1}\\ \Phi^{(4)}_{-1}\\ \Phi^{(4)}_{-3}\\ \Phi^{(5)}_{5}\\ \Phi^{(5)}_{3}\\ \Phi^{(5)}_{1}\\ \Phi^{(5)}_{-1}\\ \Phi^{(5)}_{-3}\\ \Phi^{(5)}_{-5}
\end{pmatrix}
\quad (17)
$$

Footnote: η should be replaced by $-\eta$ in Eq. (17).

Figure 2 explains these ideas. Tables 2A and 2B contain the transformation matrices that diagonalise (14) and (16). The computation of $\Phi_q^{(k)}(t)$ as a function of initial polarisations $\Phi_q^{(k)}(0)$ is straightforward.

Spin 5/2

The problem is more difficult as a result of the operator dimensionality, namely 36 × 36. However, odd − even q separation leads to two sets, an 18 × 18 matrix and a 17 × 17 matrix. We present here only the former, for brevity. Also reference to Fig. 3 suggests that the secular equation for the 18 × 18 matrix is not an eighteenth order polynomial, but reducible to a cubic equation.

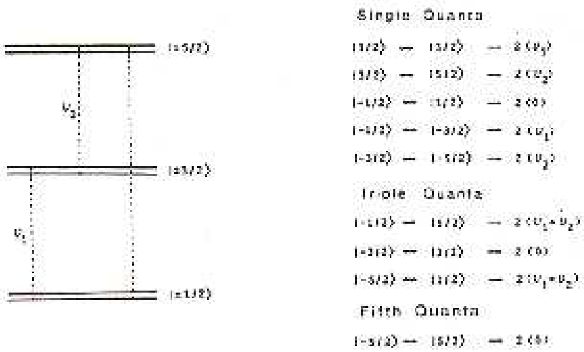

Fig. 3. Frequency spectrum of spin 5/2.

Thus, the possible eighteen frequencies are grouped into a doubly degenerate set ($\pm\nu_1, \pm\nu_2, \pm(\nu_1+\nu_2)$, 0, 0, 0). The secular equation containing these eigenvalues can be written as $[\lambda^3(\lambda^6 + a\lambda^4 + b\lambda^2 + c)]^2 = 0$ where λ is the eigenvalue. Expansions of the determinant (17) analytically using Reduce version 3.1 [7] leads to the predicted result. The secular equation is

$$\left\{\lambda^3\left[\lambda^6 + \frac{63}{50}(1+\eta^2/3)\,\lambda^4 + \frac{1}{4}\left(\frac{63}{50}\right)^2(1+\eta^2/3)^2\lambda^2 + \left(\frac{1}{500}\right)^2(6561+14661\,\eta^2+387\,\eta^4+343\,\eta^6)\right]\right\}^2 = 0\,. \quad (18)$$

The roots of the equation can be obtained in a closed form using trigonometric formulae

$$\lambda_1^2 = A^2 \times \frac{21}{50}\,(1+\eta^2/3)\left[\cos\frac{\theta}{3} - 1\right],$$

$$\lambda_2^2 = A^2 \times \frac{21}{50}\,(1+\eta^2/3)\left[\cos\left(\frac{\theta}{3} + 240°\right) - 1\right],$$

$$\lambda_3^2 = (\lambda_1+\lambda_2)^2$$
$$= A^2 \times \frac{21}{50}\,(1+\eta^2/3)\left[\cos\left(\frac{\theta}{3} + 120°\right) - 1\right]$$

or

$$\lambda_1 = \pm i\nu_1 = \pm iA\frac{\sqrt{21}}{5}\sqrt{(1+\eta^2/3)}\,\sin\theta/6,$$

$$\lambda_2 = \pm i\nu_2 = \pm iA\frac{\sqrt{21}}{5}\sqrt{(1+\eta^2/3)}\,\sin\left(\frac{\theta}{6} + 120°\right),$$

Table 2B. Tranformation matrix that diagonalises (16).

$\frac{\sqrt{5}}{\sqrt{(3\eta^2+10)}}$	0	$\frac{-(5-\eta^2)\sqrt{3}}{A_5\sqrt{5}}$	$\frac{-\eta\sqrt{6}}{A_6}$	0	$\frac{-\eta\sqrt{6}}{A_6}$	0
0	$\frac{-\eta}{\sqrt{2(\eta^2+3)}}$	0	$\frac{i\sqrt{15(\eta^2+3)}}{A_6}$	$\frac{\sqrt{3}}{2\sqrt{(\eta^2+3)}}$	$\frac{-i\sqrt{15(\eta^2+3)}}{A_6}$	$\frac{\sqrt{3}}{2\sqrt{(\eta^2+3)}}$
0	$\frac{-\sqrt{3}}{\sqrt{(\eta^2+3)}}$	0	$\frac{-i\eta\sqrt{5(\eta^2+3)}}{A_6\sqrt{2}}$	$\frac{-\eta}{\sqrt{2(\eta^2+3)}}$	$\frac{i\eta\sqrt{5(\eta^2+3)}}{A_6\sqrt{2}}$	$\frac{-\eta}{\sqrt{2(\eta^2+3)}}$
0	$\frac{-\eta}{\sqrt{2(\eta^2+3)}}$	0	0	$\frac{\sqrt{3}}{2\sqrt{(\eta^2+3)}}$	0	$\frac{\sqrt{3}}{2\sqrt{\eta^2+3}}$
$\frac{-\eta\sqrt{3}}{\sqrt{2(3\eta^2+10)}}$	0	$\frac{\eta}{A_5\sqrt{2}}$	$\frac{-\sqrt{5}(\eta^2+6)}{2A_6}$	$\frac{i}{2}$	$\frac{-\sqrt{5}(\eta^2+6)}{2A_6}$	$-\frac{i}{2}$
$\frac{\sqrt{5}}{\sqrt{(3\eta^2+10)}}$	0	$\frac{(5-2\eta^2)\sqrt{3}}{A_5\sqrt{5}}$	$\frac{-\eta\sqrt{3}}{A_6\sqrt{2}}$	0	$\frac{-\eta\sqrt{3}}{A_6\sqrt{2}}$	0
$\frac{-\eta\sqrt{3}}{\sqrt{2(3\eta^2+10)}}$	0	$\frac{\eta}{A_5\sqrt{2}}$	$\frac{\sqrt{5}\,\eta^2}{2A_6}$	$-\frac{i}{2}$	$\frac{\sqrt{5}\,\eta^2}{2A_6}$	$\frac{i}{2}$

$A_5^2 = (30 - 17\eta^2 + 3\eta^4)$; $A_6^2 = 5(\eta^2+6)(\eta^2+3)$

Table 2A. Transformation matrix that diagonalises (14).

0	$\frac{10\eta}{A_1}$	$\frac{(-16\eta^4+216)}{3\sqrt{10}A_2}$	$\frac{2\sqrt{2}(2\eta^3+3\eta)}{3\sqrt{5}A_3}$	$\frac{\eta}{\sqrt{10(\eta^2+3)}}$	$\frac{(\eta^2-9)}{\sqrt{10}A_4}$	$\frac{\eta}{\sqrt{10(\eta^2+3)}}$	$\frac{(\eta^2-9)}{\sqrt{10}A_4}$
$\frac{-\sqrt{5}\eta}{\sqrt{(7\eta^2+18)}}$	$\frac{(\eta^2+6)}{A_1}$	0	$\frac{2\sqrt{2}(2\eta^2+9)}{3\sqrt{5}A_3}$	$\frac{-3}{\sqrt{10(\eta^2+3)}}$	0	$\frac{-3}{\sqrt{10(\eta^2+3)}}$	0
0	0	0	0	0	$\frac{-3i\sqrt{(\eta^2+3)}}{\sqrt{2}A_4}$	0	$\frac{3i\sqrt{(\eta^2+3)}}{\sqrt{2}A_4}$
0	0	0	0	$\frac{i}{\sqrt{2}}$	$\frac{i\sqrt{(\eta^2+3)}}{A_4}$	$\frac{-i}{\sqrt{2}}$	$\frac{-i\sqrt{(\eta^2+3)}}{A_4}$
$\frac{-\eta\sqrt{2}}{\sqrt{(7\eta^2+18)}}$	$\frac{-\sqrt{5}(\eta^2+6)}{\sqrt{2}A_1}$	$\frac{(\eta^3+6\eta)}{A_2}$	$\frac{(5\eta^2+18)}{3A_3}$	0	$\frac{-3\eta}{2A_4}$	0	$\frac{-3\eta}{2A_4}$
0	0	$\frac{(7\eta^2+18)(\eta^2+6)}{\sqrt{15}A_2}$	$\frac{(7\eta^3+18\eta)}{3\sqrt{15}A_3}$	$\frac{\eta\sqrt{3}}{2\sqrt{5(\eta^2+3)}}$	$\frac{\sqrt{3}(\eta^2+6)}{2\sqrt{5}A_4}$	$\frac{\eta\sqrt{3}}{2\sqrt{5(\eta^2+3)}}$	$\frac{\sqrt{3}(\eta^2+6)}{2\sqrt{5}A_4}$
0	$\frac{(-7\eta^2+18)}{\sqrt{6}A_1}$	$\frac{-\sqrt{5}\eta(5\eta^2+18)}{\sqrt{3}A_2}$	$\frac{9(\eta^2+2)}{A_3\sqrt{15}}$	$\frac{\sqrt{3}}{\sqrt{5(\eta^2+3)}}$	$\frac{\sqrt{15}\eta}{2A_4}$	$\frac{\sqrt{3}}{\sqrt{5(\eta^2+3)}}$	$\frac{\sqrt{15}\eta}{2A_4}$
$\frac{3\sqrt{2}}{\sqrt{(7\eta^2+18)}}$	0	$\frac{\eta^4+6\eta^2}{3A_2}$	$\frac{(\eta^3+4\eta)}{A_3}$	$\frac{-\eta}{2\sqrt{(\eta^2+3)}}$	$\frac{-\eta^2}{2A_4}$	$\frac{-\eta}{2\sqrt{(\eta^2+3)}}$	$\frac{-\eta^2}{2A_4}$

$A_1^2=\frac{3}{5(7\eta^2+18)(\eta^2+6)}$; $A_2^2=\frac{9}{4(7\eta^2+18)(\eta^2+6)(2\eta^2+9)(\eta^2+3)}$; $A_3^2=\frac{135}{4(47\eta^4+237\eta^2+216)(2\eta^2+9)}$; $A_4^2=\frac{1}{(\eta^2+9)(\eta^2+3)}$

where

$$\cos\theta = \left[-\frac{(3861 + 20061\,\eta^2 - 2313\,\eta^4 + 343\,\eta^6)}{21^3(1 + \eta^2/3)^3} \right] \tag{19}$$

and

$$A = \bar{Q}/\hbar\,.$$

ν_1 and ν_2 are the two frequencies of the spin (5/2) system and are thus expressed analytically in terms of the electric quadrupole coupling constant and the asymmetry parameter. The transformation matrices that diagonalise (17) and its even q counterpart are not presented here because of the algebraic complexity. Exact numerical results are available from the authors. Numerical calculation of the frequencies from (19) agree exactly with the results computed from numerical values of the energy levels.

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