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Second-moment nuclear quadrupole resonance measurement of ^{127}I in $NaIO_4$

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Abstract. This work reports measurements of both homonuclear dipolar coupling and heteronuclear dipolar plus quadrupolar NQR second moments of a spin-5/2 nucleus, ^{127}I, by means of the Hahn and solid echoes sequences for $NaIO_4$. The homonuclear second-moment experimental result is compared with the theoretical expected value. In addition, a demonstration is given to show that the results are the Van Vleck moments.

1. Introduction

The present work consists essentially of two parts. One is the theoretical introduction of the density matrix method which is necessary to give an introduction and to develop an explanation of the experimental results. This first part is entirely contained in the introduction. The experimental section contains information about the sample under study, the measured data, and some considerations concerning the spectrometer performance required to obtain the desired measurements. Finally, the conclusion shows that the experimental results are in good agreement with the expected theoretical values and that the measured moments are the Van Vleck second moments.

The density matrix formalism has been proved to be particularly suitable for describing the evolution as well as the response of a spin system to a sequence of radio-frequency (RF) pulses [1, 2]. In addition, it has been shown that the spin-density operator in the interaction representation [3], for the nuclear quadrupole resonance (NQR), is very convenient as regards obtaining a general expression for the spin echoes following a pulse sequence [4, 5]. The method consists in writing all the operators of interest as linear combinations of generators of a particular basis of the Lie algebra of the SU(n) group. For the case of the NQR of spin $I = \frac{5}{2}$ the group to be considered is SU(6) [5]. The system Hamiltonian is

$$H(t) = H_Q + H_D + H_{rf}(t) \tag{1}$$

where H_D and $H_{rf}(t)$ are the dipolar and the RF Hamiltonians respectively, the latter taking account of the time perturbation needed to induce a transition between the quadrupolar levels. Finally, H_Q is the quadrupolar Hamiltonian, which is conveniently written as

$$H_Q = \sum_k \frac{1}{2}\omega_Q^k (I_0^k + \eta I_1^k) \tag{2}$$

where the index k labels the resonant nuclei, η is the electric field gradient (EFG) asymmetry parameter, and

$$I_0 = 3I_z^2 - \boldsymbol{I}^2 \qquad I_1 = \frac{1}{6}(I_+^2 + I_-^2) \qquad \omega_Q = \frac{e^2 qQ}{2I(2I-1)} \tag{3}$$

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where the parameters q and Q are the field gradient and the quadrupolar moment per unit of the electronic charge respectively.

The spin system is assumed to be initially at thermal equilibrium with its lattice at a temperature such that the high-temperature approximation is valid; thus the initial state is described by

$$\rho_0 = C\left(1 - \frac{H_Q}{k_B T}\right) \qquad -\frac{C}{k_B T} = \frac{\mathrm{Tr}\{\rho_0 H_Q\}}{\mathrm{Tr}\{H_Q^2\}} \equiv \frac{E_{0Q}}{\mathcal{H}_0^2} \tag{4}$$

where k_B is the Boltzmann constant and C is a normalization factor. Subsequently, a convenient matrix representation of the Lie algebra of the SU(6) group is obtained [5], namely a set of 35 anti-Hermitian traceless matrices, $\mathbf{V}_i$, of order 6×6, for which both an inner product and an operator expansion can be written out, as follows:

$$\langle \mathbf{A}|\mathbf{B}\rangle = \mathrm{Tr}\{\mathbf{A}\mathbf{B}^\dagger\} \qquad \mathbf{O} = \sum_{i=1}^{35} \langle \mathbf{V}_i|\mathbf{O}\rangle \mathbf{V}_i. \tag{5}$$

Thereafter, the above-mentioned operators are transformed into the interaction representation by means of the operator

$$U(t) = \exp\left\{-\mathrm{i}\sum_k \frac{1}{2}\omega_Q^k (I_0^k + \eta I_1^k)\right\}. \tag{6}$$

Thus, the dynamics of the system is now described by

$$\frac{\mathrm{d}}{\mathrm{d}t}\tilde{\rho}(t) = \mathrm{i}\hbar\left[\tilde{\rho}(t), \tilde{H}_{eff}(t)\right] \tag{7}$$

where the effective interaction Hamiltonian is

$$\tilde{H}_{eff}(t) = \sum_k \frac{1}{2}\,\Delta\omega_k\, I_0^k + H_D^0 + \tilde{H}_{rf}(t) \tag{8}$$

where it has been assumed that the parameter $\eta = 0$, $\Delta\omega_k$ takes into account the fact that different spins resonate at frequencies other than that of the centre of the line, H_D^0 is the secular part of the dipolar Hamiltonian, and $\tilde{H}_{rf}(t)$ takes the following matrix form:

$$\tilde{H}_{rf}(t) = \frac{\omega_1}{2}[\mathbf{F} + 2\mathbf{A}\cos(\omega t) - 2\mathbf{B}\sin(\omega t) + \mathbf{D}\cos(2\omega t) + \mathbf{R}\sin(2\omega t)\cos(t\omega)] \tag{9}$$

where $\mathbf{F}$, $\mathbf{B}$, $\mathbf{D}$, and $\mathbf{R}$ are matrix operators cast in terms of the matrices $\mathbf{V}_i$ [5]. The relevant contribution of (9) in the rotating frame at frequency ω_Q, i.e. under resonance conditions, is the zero-order term of the Fourier series of $\tilde{H}_{rf}$; this reduces to

$$\tilde{H}_{rf} = \frac{\omega_1}{2}\mathbf{A}. \tag{10}$$

It has also been shown [5] that after applying a resonant RF pulse of duration t_{w_1}, such that $2t_{w_1}$ fully saturates the spin response, and under the approximation of infinite RF power, the state of the spin system is described by

$$\tilde{\rho}(t_{w_1}) = -\frac{E_{0Q}}{2H_0^2}[\tilde{\omega}_0\mathbf{U} + (1 + \mathcal{O})\mathbf{B}] \tag{11}$$

where $\tilde{\omega}_0$ represents an average frequency over the NQR spectrum which for a symmetric resonance line coincides with the centre of the peak, and the factor premultiplying the second term is nearly equal to one for a narrow peak. On similar grounds the state of the system after an echo pulse sequence can be obtained either for a Hahn echo or a solid echo:

$$\tilde{\rho}(t + t_{w_2} + \tau + t_{w_1}) = \mathrm{e}^{-\mathrm{i}\tilde{H}t}\mathbf{M}\mathrm{e}^{-\mathrm{i}\tilde{H}\tau}\tilde{\rho}(t_{w_1})\mathrm{e}^{\mathrm{i}\tilde{H}\tau}\mathbf{M}^\dagger\mathrm{e}^{\mathrm{i}\tilde{H}t} \tag{12}$$

where

$$\mathbf{M} = \exp\{-\mathrm{i}\tilde{H}_{rf} t_{w_2}\}. \tag{13}$$

The matrices $\mathbf{V}_i$ as well as the matrix operators introduced above, $\mathbf{A}$, $\mathbf{B}$, $\mathbf{D}$, $\mathbf{F}$, and $\mathbf{R}$, are given explicitly in the appendix. A better understanding of what kind of role some of these operators take [5] is achieved by observing that, as in the classical picture of NMR, where in the interaction representation there is a quantization direction and two perpendicular axes ($\tilde{x}$, $\tilde{y}$, $\tilde{z}$), the matrix operators I_0, $\mathbf{A}$, and $\mathbf{B}$ are in orthogonal directions, not in real space but in a matrix space, assigned as follows:

I_0 ——— $\tilde{\boldsymbol{z}}$

$\mathbf{A}$ ——— $\tilde{\boldsymbol{x}}$

$\mathbf{B}$ ——— $\tilde{\boldsymbol{y}}$.

Once the density matrix is known, the signal following a RF pulse sequence is obtained from

$$G(t,\tau) = \mathrm{Tr}\{\tilde{\rho}(t + t_{w2} + \tau + t_{w1})\tilde{I}_T\} \tag{14}$$

where $\tilde{I}_T$ is the total projection of the spin contribution in the interaction representation, which reduces to

$$\tilde{I}_T = 2\mathbf{A}\cos(\omega t) + 2\mathbf{B}\sin(\omega t) + \mathbf{F}. \tag{15}$$

On performing a power series on t and τ of equation (10), knowing that $G(t,\tau) = G(-t,-\tau)$, an expression for the signal is obtained:

$$\begin{aligned} G(t,\tau) = {}& \frac{E_{0q}}{2\mathcal{H}_0^2}\omega_0 \sum_{n=0}^{\infty}\sum_{m=0}^{\infty} \frac{(-\mathrm{i}\tau)^n(\mathrm{i}t)^m}{\Gamma(n+1)\Gamma(m+1)} \\ & \times \mathrm{Tr}\left\{[\tilde{H},[\tilde{H},\ldots,[\tilde{H},\mathbf{B}]]]\mathbf{M}[\tilde{H},[\tilde{H},\ldots,[\tilde{H},\mathbf{B}]]]\mathbf{M}^{\dagger}\right\}. \end{aligned} \tag{16}$$

In order to decouple the homonuclear spin–spin contribution to the second moment from the heteronuclear and quadrupolar ones it is necessary to consider both the Hahn and the solid echoes. Thus we definine the moments as

$$M_2^{II} = \frac{1}{\mathrm{Tr}\{\mathbf{B}^2\}}\mathrm{Tr}\{[H_D^{II},[H_D^{II},\mathbf{B}]]\mathbf{B}\} \tag{17}$$

$$M_2^{Q+IS} = \frac{1}{\mathrm{Tr}\{\mathbf{B}^2\}}\mathrm{Tr}\{[H^{Q+IS},[H^{Q+IS},\mathbf{B}]]\mathbf{B}\}. \tag{18}$$

After some algebra, the expressions for the Hahn and the solid echoes up to second order are given respectively by

$$\begin{aligned} G_{\mathrm{Hahn}}(t,\tau) = {}& \frac{E_{0q}}{2Q^2}\omega_0\,\mathrm{Tr}\{\mathbf{B}^2\}\left\{Y - Y\frac{M_2^{II}}{2}(t+\tau)^2\right. \\ & \left. + (1-Y)\frac{M_2^{Q+IS}}{4}(t+\tau)^2 - (1+Y)\frac{M_2^{Q+IS}}{4}(t-\tau)^2 + \cdots\right\} \end{aligned} \tag{19}$$

$$\begin{aligned} G_{\mathrm{sol}}(t,\tau) = {}& -\frac{E_{0q}}{2Q^2}\omega_0\,\mathrm{Tr}\{\mathbf{B}^2\}\left\{1 - \frac{1}{4}[M_2^{II}(1-X)(t+\tau)^2 + + M_2^{II}(1+X)(t-\tau)^2\right. \\ & \left. + M_2^{Q+IS}(t+\tau)^2 + M_2^{Q+IS}(t-\tau)^2] + \cdots\right\} \end{aligned} \tag{20}$$

where the parameters Y and X may either be measured or calculated under some physical assumptions about the resonance line symmetry and the spin of the resonant nucleus. In particular, the parameter Y characterizes the effective spin flip induced by the RF. The desired value is $Y \approx 1$, for the special case where $Y = 1$ is that for which the condition of saturation is fully achieved. Similar theoretical considerations are valid for X.

The parameter Y is directly obtained by the measurement of both the Hahn and solid echoes at values of $\tau \approx 0$, and from equations (16) and (17) we have the result

$$Y = \left|\frac{G_{\mathrm{Hahn}}(0)}{G_{\mathrm{sol}}(0)}\right|. \tag{21}$$

Also, from equations (19) and (20) it is easy to obtain a linear relation on τ with both the homonuclear and heteronuclear quadrupolar second moments. Equations (22) and (23) show the linear dependence on τ of the absolute value of the derivative of the echo amplitude with respect to τ scaled relative to its value at $\tau = 0$ (in both cases it has been assumed that $Y \approx X \approx 1$):

$$\left|\frac{(\mathrm{d}/\mathrm{d}\tau)G_{\mathrm{Hahn}}(\tau,\tau)}{G_{\mathrm{Hahn}}(0,0)}\right| = 4M_2^{II}\tau \tag{22}$$

$$\left|\frac{(\mathrm{d}/\mathrm{d}\tau)G_{\mathrm{sol}}(\tau,\tau)}{G_{\mathrm{sol}}(0,0)}\right| = 2M_2^{Q+IS}\tau. \tag{23}$$

These relations allow one to measure the second moments by obtaining the amplitudes of the echo signals for different values of the pulse separation τ. Some experimental considerations must be taken into account—namely that $G_{\mathrm{Hahn}}(0)$ and $G_{\mathrm{sol}}(0)$ cannot be measured directly. This is mainly due to the coil ringing which prevents an accurate determination of the pulse duration being made for small values of τ. Therefore, only by means of an extrapolation of the echo amplitude to $\tau = 0$ can the former quantities be obtained. It is important to note that this does not involve an ordinary spin-echo experiment where after a given pulse sequence the entire signal is acquired and analysed. This method requires the sampling of just one experimental point for each value of τ, and after several measurements the moments are obtained from a plot made according to equations (19) and (20).

2. Experimental details

The compound studied on this work is $NaIO_4$ and it was purchased from Sigma. Special care was taken with the sample—that is, the handling of this compound was in a pure nitrogen atmosphere—and no recrystallization was needed. The compound crystallizes in a tetragonal C_{4h}^6 structure with the lattice parameters $a = b = 5.337$ Å and $c = 11.947$ Å [6]. The NQR measurements were performed at room temperature in a Bruker-MSL 300 spectrometer with multinuclear high-power unit and a broad-band high-power tunable probe. The $NaIO_4$ exhibits an NQR resonance at 13.220 294 MHz for ^{127}I nuclei and the electric field gradient asymmetry parameter $\eta = 0$.

Figures 1 and 2 show the echo amplitudes corresponding to Hahn and solid echo sequences, respectively, as functions of the RF-pulse separation squared, τ^2. The data clearly show two zones, one at large values of τ^2 where the echo amplitudes decay non-linearly, and the second zone at small values of τ^2 where the amplitudes behave linearly. The relevant results are listed in table 1.

The units of the data in table 1 are echo amplitude times Hz^2 for the slope, and echo amplitude for the abscissa. With these data, and using equation (21), an experimental value

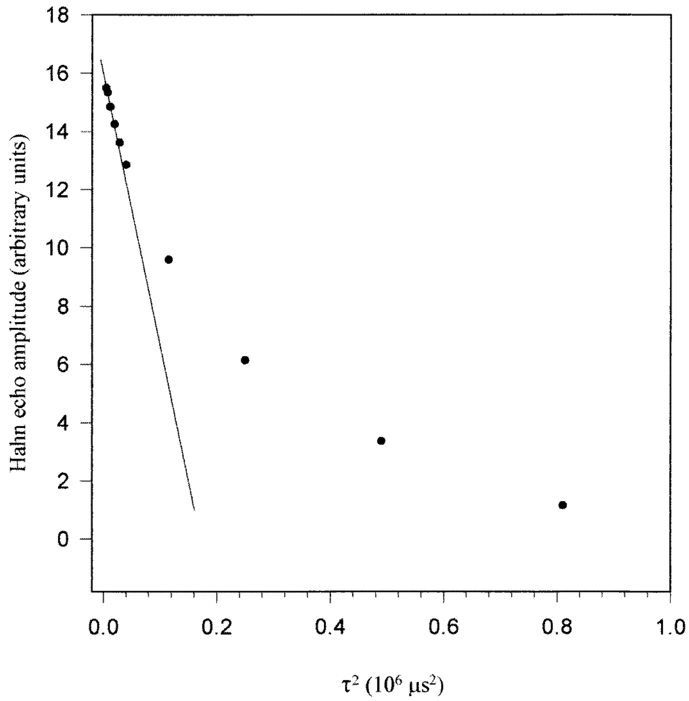

Figure 1. The Hahn echo amplitude versus τ^2.

Table 1.

	Hahn echo	Solid echo
Slope at $\tau = 0$	-7.625×10^7	-2.045×10^9
Abscissa at $\tau = 0$	15.84	14.83

of the parameter $Y \approx 1.1 \pm 0.09$ is obtained. The expected theoretical value corresponding to a symmetric and fully saturated resonance line is $Y = 1$.

With the above data, and according to equations (19) and (20), the experimental values of the homonuclear and heteronuclear plus quadrupolar second moments are respectively

$$M_2^{II} = (2.4 \pm 0.2) \times 10^6 \text{ Hz}^2 \qquad M_2^{Q+IS} = (1.4 \pm 0.2) \times 10^8 \text{ Hz}^2.$$

The derivation of the above parameters is based upon the assumption that moments of order higher than two do not contribute to the series expansion of equations (17) and (18). In order to make an estimation, and for the sake of simplicity, let us assume that the resonance line is well described by a Gaussian profile. For such a symmetric line the free-induction decay signal following a single $\pi/2$ RF pulse is given by

$$G(\tau) = G(0) - \frac{1}{2}M_2\tau^2 + \frac{1}{16}M_4\tau^4 - \cdots \tag{24}$$

where the second and fourth moments are related to the linewidth $\Delta\omega$ by

$$M_2 = \left(\frac{1}{1.18}\right)^2 \Delta\omega^2 \qquad M_2 = 3\left(\frac{1}{1.18}\right)^4 \Delta\omega^4. \tag{25}$$

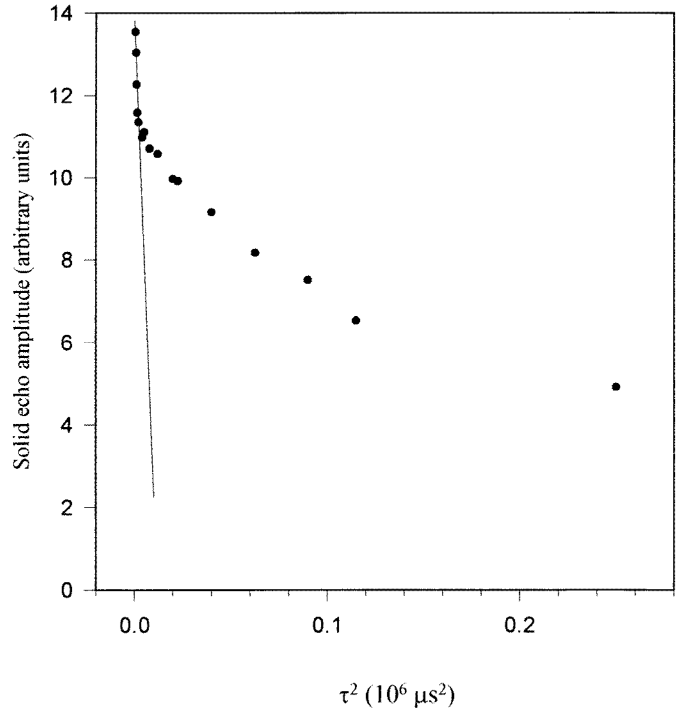

Figure 2. The solid echo amplitude versus τ^2.

In order to drop the fourth-moment term from equation (22), it is desirable that the ratio

$$\left|\frac{\frac{1}{16}M_4\tau^4}{\frac{1}{2}M_2\tau^2}\right| < 10^{-2}. \qquad (26)$$

It follows that $\Delta\omega\,\tau < 0.2$, and assuming that the spectrometer dead time following an RF pulse is of the order of 30 μs, the desired NQR linewidth should be $\Delta\omega \approx 7$ kHz. These results imply that for relatively narrow resonance lines the contribution of the dropped term to the echo is of the order of 1% and all previous extrapolations of the echo amplitudes to $\tau = 0$ are valid. It must be pointed out that the broader the resonance line, the greater the number of terms in the expansions of equations (17) and (18) that should be considered.

3. Conclusions

Taken together with previous theoretical calculations of second moments of pure NQR spin echoes for nuclei with spin $\frac{5}{2}$ [5], the present work shows that their experimental values are obtained by means of two pulse sequences, namely the Hahn and the solid echo ones. The values of M_2^{II} and M_2^{Q+IS} are measured with errors of 9% and 14% respectively. As a way of making a comparison, a theoretical value of M_2^{II} is obtained from a first-principles calculation of Van Vleck's homonuclear second moment [7], in terms of the crystal lattice parameters [8]. This is given by

$$M_2^{II} = g^4\beta^4 \sum_j r_{jk}^{-6}\left[\left(\frac{623}{24} + 4\beta_{jk}^2\right) - \left(\frac{99}{16} + 12\beta_{jk}^2\right)\gamma_{jk}^2 + \frac{69}{16}\gamma_{jk}^4\right] \qquad (27)$$

where the direction cosines and distances between iodine nearest neighbours in $NaIO_4$ are

$$\beta_{12} = -\beta_{13} = 0 \qquad \gamma_{12} = \gamma_{13} = 0.7457 \qquad r_{12} = r_{13} = 4.0052 \text{ Å}.$$

The homonuclear second-moment value obtained from equation (27) is

$$M_2^{II} = 2.3068 \times 10^6 \text{ Hz}^2.$$

This number is in very good agreement with measured value. However, a question that has not been answered in previous publications is that of whether the measured moments, obtained by the method reported in this work, are Van Vleck's moments. In order to provide an answer let us consider the following. Firstly, from equation (10), where we have set the values of t_{w2} and t equal to zero, the density matrix at a time τ after the first RF pulse is

$$\tilde{\rho}(\tau) \propto \mathbf{U}(\tau) - \mathbf{B}(\tau). \tag{28}$$

Next, taking into consideration the fact that the NQR signal is detected in quadrature with the RF pulse and taking into account equation (13) in the interaction representation,

$$\tilde{\mathbf{I}}_T \propto \mathbf{B} \tag{29}$$

where $\mathbf{B} \equiv \mathbf{B}(\tau = 0)$. This allows to calculate the free-induction decay (FID) up to a constant of proportionality as follows:

$$G(\tau) \propto \mathrm{Tr}\{\tilde{\rho}(\tau)\tilde{\mathbf{I}}_T\} = \langle \mathbf{U}(\tau)|\mathbf{B}\rangle - \langle \mathbf{B}(\tau)|\mathbf{B}\rangle\,. \tag{30}$$

Assuming that $\mathbf{U}(\tau = 0) \perp \mathbf{B}$, for very short times the following relation is valid:

$$\left| \frac{\langle \mathbf{U}(\tau \sim 0)|\mathbf{B}\rangle}{\langle \mathbf{B}(\tau \sim 0)|\mathbf{B}\rangle} \right| \ll 1. \tag{31}$$

This allows to write the FID as

$$\begin{aligned} G(\tau) \propto \langle \mathbf{B}(\tau)|\mathbf{B}\rangle &= \|\mathbf{B}^2\| - \mathrm{i}\langle [H_Q + H_D^0, \mathbf{B}]|\mathbf{B}\rangle\tau \\ &\quad - \frac{1}{2!}\langle [H_Q + H_D^0, [H_Q + H_D^0, \mathbf{B}]]|\mathbf{B}\rangle\tau^2 + \cdots. \end{aligned} \tag{32}$$

Therefore, within the range of validity of equation (29) and assuming that the signal amplitude detected is for values of $\tau \simeq 0$ and that the data are extrapolated to their values for $\tau = 0$, the moments are given by

$$M_n = \frac{\langle \overbrace{[H_Q + H_D^0, [H_Q + H_D^0, \cdots, [H_Q + H_D^0, \mathbf{B}]]\cdots]}^{n \text{ times}}\,|\mathbf{B}\rangle}{\|\mathbf{B}\|^2}. \tag{33}$$

This equation shows that the moments given by equations (15) and (16) are Van Vleck moments.

Acknowledgments

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Appendix

Here, we give the matrix presentation of the Lie algebra of the SU(6) group:

$$\mathbf{V}_1 = \frac{1}{2\sqrt{3}}\begin{pmatrix} 1&0&0&0&0&0\\ 0&1&0&0&0&0\\ 0&0&\bar{2}&0&0&0\\ 0&0&0&\bar{2}&0&0\\ 0&0&0&0&1&0\\ 0&0&0&0&0&1 \end{pmatrix} \qquad \mathbf{V}_2 = \frac{1}{2}\begin{pmatrix} 1&0&0&0&0&0\\ 0&\bar{1}&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&\bar{1}&0\\ 0&0&0&0&0&1 \end{pmatrix}$$

$$\mathbf{V}_3 = \frac{1}{2}\begin{pmatrix} 1&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&1&0&0&0\\ 0&0&0&\bar{1}&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&\bar{1} \end{pmatrix} \qquad \mathbf{V}_4 = \frac{1}{2}\begin{pmatrix} 1&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&1&0&0&0\\ 0&0&0&\bar{1}&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&\bar{1} \end{pmatrix}$$

$$\mathbf{V}_5 = \frac{1}{\sqrt{2}}\begin{pmatrix} 0&0&0&0&0&0\\ 0&1&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&\bar{1}&0\\ 0&0&0&0&0&0 \end{pmatrix} \qquad \mathbf{V}_6 = \frac{1}{2}\begin{pmatrix} 0&1&0&0&0&0\\ 1&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&\bar{1}\\ 0&0&0&0&\bar{1}&0 \end{pmatrix}$$

$$\mathbf{V}_7 = \frac{1}{2}\begin{pmatrix} 0&0&1&0&0&0\\ 0&0&0&0&0&0\\ 1&0&0&0&0&0\\ 0&0&0&0&0&\bar{1}\\ 0&0&0&0&0&0\\ 0&0&0&\bar{1}&0&0 \end{pmatrix} \qquad \mathbf{V}_8 = \frac{1}{2}\begin{pmatrix} 0&0&0&1&0&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&\bar{1}\\ 1&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&0&\bar{1}&0&0&0 \end{pmatrix}$$

$$\mathbf{V}_9 = \frac{1}{2}\begin{pmatrix} 0&0&0&0&1&0\\ 0&0&0&0&0&\bar{1}\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 1&0&0&0&0&0\\ 0&\bar{1}&0&0&0&0 \end{pmatrix} \qquad \mathbf{V}_{10} = \frac{1}{2}\begin{pmatrix} 0&0&0&0&0&1\\ 0&0&0&0&1&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&1&0&0&0&0\\ 1&0&0&0&0&0 \end{pmatrix}$$

$$\mathbf{V}_{11} = \frac{1}{2}\begin{pmatrix} 0&0&0&0&0&0\\ 0&0&1&0&0&0\\ 0&1&0&0&0&0\\ 0&0&0&0&\bar{1}&0\\ 0&0&0&\bar{1}&0&0\\ 0&0&0&0&0&0 \end{pmatrix} \qquad \mathbf{V}_{12} = \frac{1}{2}\begin{pmatrix} 0&0&0&0&0&0\\ 0&0&0&1&0&0\\ 0&0&0&0&\bar{1}&0\\ 0&1&0&0&0&0\\ 0&0&\bar{1}&0&0&0\\ 0&0&0&0&0&0 \end{pmatrix}$$

$$\mathbf{V}_{13} = \frac{1}{2}\begin{pmatrix} 0&0&0&0&0&\bar{1}\\ 0&0&0&0&1&0\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 0&1&0&0&0&0\\ \bar{1}&0&0&0&0&0 \end{pmatrix} \qquad \mathbf{V}_{14} = \frac{1}{2}\begin{pmatrix} 0&0&0&0&1&0\\ 0&0&0&0&0&1\\ 0&0&0&0&0&0\\ 0&0&0&0&0&0\\ 1&0&0&0&0&0\\ 0&1&0&0&0&0 \end{pmatrix}$$

$$\mathbf{V}_{15} = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \qquad \mathbf{V}_{16} = \frac{1}{2}\begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

$$\mathbf{V}_{17} = \frac{1}{2}\begin{pmatrix} 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \end{pmatrix} \qquad \mathbf{V}_{18} = \frac{1}{2}\begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

$$\mathbf{V}_{19} = \frac{1}{2}\begin{pmatrix} 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \end{pmatrix} \qquad \mathbf{V}_{20} = \frac{1}{2}\begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \end{pmatrix}$$

$$\mathbf{V}_{21} = \frac{\mathrm{i}}{2}\begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ \bar{1} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & \bar{1} & 0 \end{pmatrix} \qquad \mathbf{V}_{22} = \frac{\mathrm{i}}{1}\begin{pmatrix} 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ \bar{1} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \bar{1} & 0 & 0 \end{pmatrix}$$

$$\mathbf{V}_{23} = \frac{\mathrm{i}}{2}\begin{pmatrix} 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ \bar{1} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \bar{1} & 0 & 0 & 0 \end{pmatrix} \qquad \mathbf{V}_{24} = \frac{\mathrm{i}}{2}\begin{pmatrix} 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ \bar{1} & 0 & 0 & 0 & 0 & 0 \\ 0 & \bar{1} & 0 & 0 & 0 & 0 \end{pmatrix}$$

$$\mathbf{V}_{25} = \frac{\mathrm{i}}{2}\begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \bar{1} & 0 & 0 & 0 & 0 \\ \bar{1} & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \qquad \mathbf{V}_{26} = \frac{\mathrm{i}}{2}\begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & \bar{1} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & \bar{1} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

$$\mathbf{V}_{27} = \frac{\mathrm{i}}{2}\begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & \bar{1} & 0 & 0 & 0 & 0 \\ 0 & 0 & \bar{1} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \qquad \mathbf{V}_{28} = \frac{\mathrm{i}}{2}\begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & \bar{1} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ \bar{1} & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

$$\mathbf{V}_{29} = \frac{\mathrm{i}}{2}\begin{pmatrix} 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & \bar{1} \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ \bar{1} & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \end{pmatrix} \qquad \mathbf{V}_{30} = \frac{\mathrm{i}}{\sqrt{2}}\begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & \bar{1} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

$$\mathbf{V}_{31} = \frac{\mathrm{i}}{2}\begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & \bar{1} & 0 \\ 0 & \bar{1} & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \qquad \mathbf{V}_{32} = \frac{\mathrm{i}}{2}\begin{pmatrix} 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \bar{1} \\ \bar{1} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \end{pmatrix}$$

$$\mathbf{V}_{33} = \frac{\mathrm{i}}{2}\begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & \bar{1} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \bar{1} & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \qquad \mathbf{V}_{34} = \frac{\mathrm{i}}{2}\begin{pmatrix} 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ \bar{1} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \bar{1} \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \end{pmatrix}$$

$$\mathbf{V}_{35} = \frac{\mathrm{i}}{2}\begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ \bar{1} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \bar{1} \\ 0 & 0 & 0 & 0 & 1 & 0 \end{pmatrix}.$$

The matrix operators $\mathbf{A}$, $\mathbf{B}$, $\mathbf{D}$, $\mathbf{F}$, and $\mathbf{R}$ are given by

$$\mathbf{A} = \sqrt{2}\sum_k(\alpha_k\mathbf{V}_{18} - \gamma_k\mathbf{V}_{26})$$

$$\mathbf{B} = \sqrt{2}\sum_k(\alpha_k\mathbf{V}_{33} + \gamma_k\mathbf{V}_{11})$$

$$\mathbf{D} = \sqrt{5}(\mathbf{V}_{20} - \mathbf{V}_{21})$$

$$\mathbf{F} = \sum_k\left[\frac{3}{\sqrt{2}}\alpha_k\mathbf{V}_{15} - \frac{3}{\sqrt{2}}\gamma_k\mathbf{V}_{30} + \delta_k\left(3\mathbf{V}_3 + 2\mathbf{V}_4 + \frac{3}{\sqrt{2}}\mathbf{V}_5\right)\right]$$

$$\mathbf{R} = -\sqrt{5}(\mathbf{V}_{35} + \mathbf{V}_6)$$

where α_k, γ_k, and δ_k are the angular functions of the direction cosines of the principal-axes system at the resonant nucleus k.

References

[1] Slichter C P 1990 *Principles of Magnetic Resonance* 3rd edn (Berlin: Springer)
[2] Ernst R R, Bodenhausen G and Wokaun A 1990 *Principles of NMR in One and Two Dimensions* (Oxford: Clarendon)
[3] Pratt J P 1977 *Mol. Phys.* **34** 2539
[4] Su S and Armstrong R L 1993 *J. Magn. Reson.* A **101** 265
[5] Nagel O A, Ramia M E and Martín C A 1995 *Physica* A **218** 487
[6] 1982 *Acta Crystallogr.* B **24** 1968
[7] Van Vleck J H and Ollom J F 1951 *Physica* **17** 205
[8] Nagel O A, Ramia M E and Martín C A 1997 *Appl. Magn. Reson.* **11** 557