

From nuclear structure to the quadrupolar NMR interaction and high-resolution spectroscopy

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Received 7 September 2004

Keywords: Nuclear structure and spin; Quadrupolar coupling; Nuclear quadrupole moment; Electric field gradient; Solid-state NMR; MQMAS; STMAS; DAS; DOR; NQR

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1. Introduction

NMR spectroscopy of isotopes with nuclear spin quantum numbers greater than $1/2$ has received wide popularity recently due to the development of powerful high-resolution techniques. The theoretical description of these experiments is well established and many review articles discuss the appearance of the quadrupolar interaction in NMR spectra. In this context, however, the physical origin of the quadrupolar interaction is rarely discussed, and the quadrupolar NMR Hamiltonian is usually not derived from more fundamental principles.

The authoritative texts of Abragam [1] and Slichter [2] remain the only relevant references in this respect. On the other hand, they use spherical and spatial tensor formalisms which are not in line with recent literature, which often can cause confusion over the correct definition of quadrupolar parameters. This may have contributed to the widespread use of different conventions for the quadrupolar interaction (ω_Q , C_Q , χ , etc.), and often disguises the contributions of the nuclear and electronic effects to the quadrupolar coupling. It is the aim of this review to provide a link from nuclear physics aspects to the actual manifestation in NMR spectra. The use of modern spherical tensor definitions and SI units will help the reader to make this connection more easily and to make a comparison with recent literature more transparent.

It is not unusual that significant differences in nuclear quadrupole moment data are reported and NMR spectroscopy may be very helpful in providing more accurate data. A clear connection between NMR observables and nuclear and electronic quadrupole moment data is therefore highly valuable, especially in view of the wide variety of conventions used in the nuclear physics literature.

To pay tribute to the success of new high-resolution NMR techniques for the study of quadrupolar nuclei, a section on the most important of these experiments is included, outlining the equations for their theoretical description. This part is kept brief to avoid overlap with recent review articles, and references are given that discuss these techniques in more detail. A number of topics that are often left out, such as nuclear quadrupole resonance,

overtone spectroscopy, and the ionic model for the calculation of electric field gradients, are included.

The article is organized as follows. We provide a brief introduction into nuclear structure and spin, followed by the derivation of the quadrupolar NMR Hamiltonian via the multipole moments. The appearance of simple spectra under the action of the quadrupolar NMR Hamiltonian is then discussed, including first- and second-order effects, as well as, the nuclear quadrupole resonance case, rapid sample spinning, nutation and overtone spectroscopy, and cross-terms with the dipolar and chemical shift anisotropy interactions are given. The high-resolution techniques are then discussed, including double rotation, dynamic-angle spinning, multiple-quantum magic-angle spinning, and satellite transition magic-angle spinning.

2. Nuclear structure and nuclear and electronic multipole moments

2.1. Nuclear structure and spin

The nuclear spin responsible for NMR phenomena is the result of the interplay between the individual spins and angular momenta of the protons and neutrons that reside in the nucleus. While exact calculations of the states of different nuclides are rather difficult, models based on simplified potentials may describe the nuclear configurations to various degrees of accuracy. It is found that nuclides with certain numbers of protons and neutrons are particularly stable, namely those with numbers of particles of one kind of 2, 8, 20, 28, 50, 82, and higher [3]. These numbers are often referred to as magic numbers and can be compared in significance to the numbers of electrons in closed-shell atoms and ions (noble-gas arrangement: 2, 8, 18, ...). Nuclides in which both the numbers of neutrons and protons are 'magic' are called 'doubly magic' nuclides and are known to be exceptionally stable. The sequence of these numbers can be explained by a so-called shell model, which treats the nucleons as particles occupying orbits influenced by the average strong attractive forces exerted by the other nucleons. As one adds protons or neutrons to the nucleus

they drop into the lowest-energy shells permitted by the Pauli-Principle. Filled shells have a total angular momentum I equal to zero, and the next added nucleon (a valence nucleon) determines the I of the new ground state. To a very good approximation, one can fill up the shells first individually by protons and neutrons, and then couple the total angular momenta of both types of valence nucleons.

The nuclear spin can be calculated by examining the coupling of the individual spins of all valence nucleons. Unlike electrons, nucleons tend to pair their spins rather than to fill the orbitals according to Hund's rule. This is due to relativistic spin–orbit couplings, which also occur for electrons in heavy atoms. Since pairs couple to spin zero, a nuclide with an even number of protons and an even number of neutrons usually has spin zero.

The final spin value of a nuclide is usually determined by the spins of the unpaired protons and neutrons if any. If there is an odd number of one type of nucleons and an even number of the other, the spin is determined by the last nucleon added of the former type and is a half-integer value ($l + s$ by spin–orbit coupling). If the number of both types of nucleons is odd then proton–neutron spin coupling occurs. Whether they couple in a parallel or antiparallel manner is difficult to predict but the total spin value will be an integer value. Chapter 1 of Ref. [4] and Chapter 26 of Ref. [5] are recommended for a very instructive introduction into nuclear structure.

The following subsections are partly based on material from Abragam [1], Slichter [2], and Cohen and Reif [6], using a more common spherical tensor formalism and SI units.

2.2. The classical nucleus–electron interaction

Classically, the collective electrostatic energy from two charge distributions, $\rho_n(\mathbf{r}_n)$ for the nucleus, and $\rho_e(\mathbf{r}_e)$ for the electrons, is

$$E = \frac{1}{4\pi\epsilon_0} \iint d\mathbf{r}_e d\mathbf{r}_n \frac{\rho_e(\mathbf{r}_e)\rho_n(\mathbf{r}_n)}{|\mathbf{r}_e - \mathbf{r}_n|} \quad (1)$$

This can be expanded in spherical coordinates (r_n, θ_n, ϕ_n for the nucleus, and r_e, θ_e, ϕ_e for the electrons) using

$$\frac{1}{|\mathbf{r}_e - \mathbf{r}_n|} = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{1}{2l+1} \frac{r_{\text{small}}^l}{r_{\text{large}}^{l+1}} Y_l^{m*}(\theta_n, \phi_n) Y_l^m(\theta_e, \phi_e) \quad (2)$$

where Y_l^m are the spherical harmonics, and r_{small} and r_{large} are the smaller and the larger of the numbers r_e and r_n . Since the nucleus is so much smaller than average electron distances, we can safely assume that $r_{\text{small}} = r_n$ and $r_{\text{large}} = r_e$. For compactness we can rewrite the energy as

$$E = \sum_{l=0}^{\infty} \sum_{m=-l}^l A_l^m B_l^{m*} \quad (3)$$

where

$$A_l^m = \sqrt{\frac{4\pi}{2l+1}} \int d\mathbf{r}_n \rho_n(r_n) r_n^l Y_l^m(\theta_n, \phi_n) \quad (4)$$

and

$$B_l^m = \frac{1}{4\pi\epsilon_0} \sqrt{\frac{4\pi}{2l+1}} \int d\mathbf{r}_e \rho_e(r_e) r_e^{-l-1} Y_l^m(\theta_e, \phi_e) \quad (5)$$

It is useful to include the factor $1/(4\pi\epsilon_0)$ in the electronic portion as it allows one to incorporate that factor into the expression for the electrostatic potential.

2.3. The quantum nucleus–electron interaction

In order to perform the transition to quantum mechanics, we make use of the correspondence principle. $r_{e,n}$, Y_l^m , and $\rho_{e,n}$ become operators and A_l^m and B_l^m expectation values. For ρ_n we use, in particular

$$\rho_n(r_n) = \left\langle \Psi_n \left| \sum_{i=1}^A e_i \delta(r_n - R_i) \right| \Psi_n \right\rangle \quad (6)$$

where $|\Psi_n\rangle$ is the ground state wave function of the nucleus, A is the number of nucleons, and

$$e_i = \begin{cases} e, & \text{the unit charge, for proton} \\ 0, & \text{for neutron} \end{cases} \quad (7)$$

A similar expression holds for the electrons, and the operators producing the expectation values A_l^m and B_l^m can then be written as

$$A_{l,m} = \sqrt{\frac{4\pi}{2l+1}} \sum_{i=1}^A e_i r_i^l Y_l^m(\theta_i, \phi_i) \quad (8)$$

$$B_{l,m} = -e \frac{1}{4\pi\epsilon_0} \sqrt{\frac{4\pi}{2l+1}} \sum_{i=1}^N r_i^{-l-1} Y_l^m(\theta_i, \phi_i) \quad (9)$$

summing over the A nucleons and N electrons, respectively. Here, r_i and Y_l^m are operators. $A_{l,m}$ and $B_{l,m}$ are spherical tensor operators of rank l and order m .

The Hamiltonian becomes a contraction of the two spherical tensors

$$H = \sum_{l=0}^{\infty} \sum_{m=-l}^l A_{l,m} B_{l,m}^\dagger = \sum_{l=0}^{\infty} \sum_{m=-l}^l (-1)^m A_{l,m} B_{l,-m} \quad (10)$$

2.4. The multipole moment representation, spherical tensors

The first term in the series is $A_{0,0}B_{0,0}$, which represents the electrostatic energy between two concentrically arranged spherically symmetric charges and is hence isotropic. Stationary nuclear states are generally assumed to have defined parity [1,3], i.e. they are unchanged under inversion of the coordinate system. This appears to be well established by experiment.

Since under the inversion P

$$(r, \theta, \phi) \xrightarrow{P} (r, \pi - \theta, \pi + \phi), \quad (11)$$

and

$$Y_l^m(\phi - \theta, \pi + \phi) \xrightarrow{P} (-1)^l Y_l^m(\theta, \phi) \quad (12)$$

all terms $A_{l,m}$ with l odd vanish.

The first relevant term is therefore the quadrupole moment ($A_{2,m}$). All moments in Eq. (10) carry a factor proportional to r_n^l/r_e^{l+1} and since $r_n \ll r_e$ the expansion converges rapidly. For this reason, the next relevant term, the hexadecapole moment, would be extremely difficult to observe [7–9]. The extent to which higher multipole moments occur is further limited by the spin value I . By the Wigner–Eckart theorem [10,11] the matrix elements of a spherical tensor operator can be written as

$$\langle I' M' | A_{l,m} | I M \rangle = \langle l m; I M | I' M' \rangle \langle I' || A_l || I \rangle \quad (13)$$

where the first factor on the right side is the Clebsch–Gordan coefficient, I the total angular momentum quantum number (corresponding to the nuclear spin), M the magnetic quantum number, and $\langle I' || A_l || I \rangle$ a constant characteristic of the particular tensor chosen, also called the ‘reduced matrix element’. The possible values of M and M' are $-I, \dots, I$. The Clebsch–Gordan factors are non-zero only for

$$|I - I'| \leq l \leq |I + I'| \quad (14)$$

hence they are zero whenever $l > 2I$. The quadrupole moment is therefore only observable for spins $I \geq 1$ and the hexadecapole moment would be seen only for $I \geq 2$.

Using the expansions of the spherical harmonics in Cartesian coordinates [10,11] one obtains

$$A_{2,0} = \frac{1}{2} \sum_i e_i (3z_i^2 - r_i^2) \quad (15)$$

$$A_{2,\pm 1} = \mp \sqrt{\frac{3}{2}} \sum_i e_i z_i (x_i \pm i y_i) \quad (16)$$

$$A_{2,\pm 2} = \sqrt{\frac{3}{8}} \sum_i e_i (x_i \pm i y_i)^2 \quad (17)$$

The quadrupole moment of the nucleus is defined as

$$eQ = \left\langle I I \left| \sum_i e_i (3z_i^2 - r_i^2) \right| I I \right\rangle = 2 \langle I I | A_{2,0} | I I \rangle \quad (18)$$

which is a number that is usually derived from experiment. The second entry in the ket means that the magnetic quantum number $M=I$. Only one constant need to be specified in Eq. (18) since all the components of the $A_{2,m}$ tensor are related to this parameter via the Wigner–Eckart Theorem. As is apparent from Eq. (18), the actual strength of the interaction depends on the state of the ensemble of the nucleons. This expression may be converted into a more

useful form by replacing $A_{2,m}$ by a tensor $Q_{2,m}$ that involves the total spin-operators only of the coupled ensemble of nucleons. Again, making use of the Wigner–Eckart Theorem, we obtain

$$Q_{2,0} = \alpha \frac{1}{2} (3I_z^2 - I(I+1)) \quad (19)$$

$$Q_{2,\pm 1} = \mp \alpha \sqrt{\frac{3}{8}} (I_z I_{\pm} + I_{\pm} I_z) \quad (20)$$

$$Q_{2,\pm 2} = \alpha \sqrt{\frac{3}{8}} I_{\pm}^2, \quad (21)$$

where the factor α is to be determined. Here

$$I_{\pm} = I_x \pm i I_y. \quad (22)$$

Occasionally, this equation is represented using the same $I_{\pm}$ symbols denoting the spherical tensor operators $T_{\pm} = \mp (1/\sqrt{2})(I_x \pm i I_y)$, in which case $Q_{2,\pm 1}$ and $Q_{2,\pm 2}$ acquire additional factors of $\mp\sqrt{2}$ and 2, respectively. We will continue to use the definition of Eq. (22).

The factor α of Eq. (19) is to be determined by introducing a number eQ , defined by

$$\begin{aligned} \langle I I | A_{2,0} | I I \rangle &= eQ/2 = \alpha \langle I I | Q_{2,0} | I I \rangle \\ &= \alpha \left\langle I I \left| \frac{1}{2} [3I_z^2 - I(I+1)] \right| I I \right\rangle \\ &= (\alpha/2) I(2I-1) \end{aligned} \quad (23)$$

which gives

$$\alpha = \frac{eQ}{I(2I-1)}. \quad (24)$$

2.5. The electric field gradient

Likewise, we can derive a spherical tensor operator for the electronic portion of the form

$$B_{2,0} = \frac{1}{2} \frac{1}{4\pi\epsilon_0} \int_{i=1}^N \frac{(-e)(3z_i^2 - r_i^2)}{r_i^5} \quad (25)$$

along with the other components.

If $V(x,y,z)$ is the electrostatic potential produced by the electrons at point (x,y,z)

$$B_{2,0} = \frac{1}{2} \left(\frac{\partial^2 V}{\partial z^2} \right)_{r=0} = \frac{1}{2} V_{zz}. \quad (26)$$

V_{zz} is an electron operator with a corresponding expectation value. The other components are

$$B_{2,\pm 1} = \mp \frac{1}{\sqrt{6}} (V_{xz} \pm i V_{yz}) \quad (27)$$

$$B_{2,\pm 2} = \frac{1}{2\sqrt{6}} (V_{xx} - V_{yy} \pm 2i V_{xy}). \quad (28)$$

If we choose as coordinate axes, the principal axes of the symmetric tensor V_{ij} , the cross-terms vanish, i.e. $V_{xy} = V_{xz} = V_{yz} = 0$. It is a common convention to label the remaining components such that

$$|V_{zz}| \geq |V_{yy}| \geq |V_{xx}| \quad (29)$$

and to define

$$V_{zz} = eq \quad (30)$$

$$\eta = (V_{xx} - V_{yy})/V_{zz}. \quad (31)$$

By Lagrange's Equation, $V_{xx} + V_{yy} + V_{zz} = 0$, and hence $|V_{zz}| = |V_{xx} + V_{yy}|$, which, combined with Eq. (29) shows that V_{xx} and V_{yy} must have the same sign, opposite to the sign of V_{zz} . Eq. (31) then shows that $0 \leq \eta \leq 1$.

Using these definitions, the tensor components for the electronic portion become

$$B_{2,0} = \frac{1}{2}eq \quad (32)$$

$$B_{2,\pm 1} = 0 \quad (33)$$

$$B_{2,\pm 2} = \frac{1}{2\sqrt{6}}eq\eta. \quad (34)$$

in the principal axis frame.

2.6. Ionic model for electric field gradients, Sternheimer factor

The calculation of the electric field gradients $V_{\alpha\alpha}$ by ab initio methods can be very time-consuming and an acceptable precision is not always achievable even using high-performance computers. Frequently, it is therefore convenient to use a point-charge approximation to calculate the field gradient produced at the site of the nucleus of interest by the surrounding charged atoms [12]. One first calculates the partial charges of the atoms surrounding the quadrupolar nucleus (these could be Mulliken charges, for example, or other types of charge interpolations). In order to calculate $eq = V_{zz}$ and $\eta = (V_{xx} - V_{yy})/V_{zz}$ one needs to first calculate $V_{\alpha\beta}^{\text{LAB}}$ in the laboratory frame. By explicit differentiation of the electrical potential of the point charges (with charge $n_i e$) one obtains

$$V_{\alpha\alpha}^{\text{LAB}} = \frac{1}{4\pi\epsilon_0} \sum_i n_i e (3\alpha_i^2 - r_i^2)/r_i^5 \quad (35)$$

$$V_{\alpha\beta}^{\text{LAB}} = \frac{1}{4\pi\epsilon_0} \sum_i n_i e 3\alpha_i \beta_i / r_i^5 \quad (36)$$

Diagonalizing the associated matrix produces $V_{\alpha\alpha}^{\text{PAS}} = V_{\alpha\alpha}$ in the principal axis frame and the corresponding transformation matrix.

In practice one finds, however, that the actual field gradient at the site of the nucleus of interest is a multiple of

the one calculated by Eq. (35) and is written as

$$V_{\alpha\alpha}^{\text{actual}} = (1 - \gamma)V_{\alpha\alpha}^{\text{calc}}. \quad (37)$$

where γ is called the Sternheimer antishielding factor [1,2]. The factors are often large and negative for heavy atoms (as large as several hundred). This effect is caused by the polarization of the closed-shell electrons in the presence of external field gradients.

3. NMR Hamiltonian and spectra

3.1. NMR Hamiltonian for the quadrupolar interaction

Combining Eqs. (10), (19)–(21), (24), (32)–(34) one arrives at the definition of the quadrupolar interaction in the principal axis frame of $V_{\alpha\beta}$ as

$$H_Q = \frac{e^2 q Q}{4I(2I - 1)} \left[3I_z^2 - I(I + 1) + \frac{\eta}{2}(I_+^2 + I_-^2) \right] \quad (38)$$

in units of Joules.

In NMR literature, it is common practice to rewrite Eq. (38) for the quadrupolar interaction as

$$H_Q = \omega_Q \sum_{m=-2}^2 (-1)^m R_{2,-m} T_{2,m} \quad (39)$$

where

$$\omega_Q = \frac{e^2 q Q}{2I(2I - 1)\hbar} = \frac{2\pi C_Q}{2I(2I - 1)}. \quad (40)$$

In this notation, H_Q and ω_Q have units of radians, and $C_Q = e^2 q Q / \hbar$, often referred to as the 'quadrupole coupling constant', has units of Hertz. The spatial tensors $R_{2,m}$ can be related to the tensors of the principal axis frame, $\rho_{l,m'}$ by a Wigner rotation parameterized by the Euler angles α, β, γ [10,11]

$$R_{l,m} = \sum_{m'} D_{m',m}^l(\alpha, \beta, \gamma) \rho_{l,m'}, \quad (41)$$

with

$$\rho_{2,0} = \sqrt{\frac{3}{2}}, \quad \rho_{2,\pm 1} = 0, \quad \rho_{2,\pm 2} = \frac{1}{2}\eta. \quad (42)$$

The spin tensors $T_{2,m}$ are defined in analogy to Eq. (19) as

$$T_{2,0} = \frac{1}{\sqrt{6}} [3I_z^2 - I(I + 1)], \quad (43)$$

$$T_{2,\pm 1} = \mp \frac{1}{2}(I_{\pm} I_z + I_z I_{\pm}), \quad T_{2,\pm 2} = \frac{1}{2} I_{\pm}^2.$$

If spherical tensors are used for $I_{\pm}$ rather than the definition of Eq. (22), additional factors of $\mp\sqrt{2}$ and 2 apply for $T_{2,\pm 1}$ and $T_{2,\pm 2}$, respectively.

The advantages of the choice of the normalizations in the R and T tensors are not immediately clear but reflect a very common convention in recent literature (one may point out

that in this convention the Clebsch–Gordan coefficient $\langle 10; 10|20\rangle = \sqrt{3/2} = \rho_{2,0}$, which highlights the fact that the second rank tensor can be produced by coupling two one-rank tensors).

In the principal axis system, Eq. (39) takes on the form

$$H_Q = (\omega_Q/2) \left\{ 3I_z^2 - I(I+1) + \frac{\eta}{2}(I_+^2 + I_-^2) \right\}. \quad (44)$$

Often, another notation is used in which $\omega'_Q = (3e^2qQ)/2I(2I-1)\hbar$. This quantity then corresponds to the distance between resonance lines in a zero-field experiment or in a high-field experiment with $\eta=0$. To avoid confusion, we denote this quantity converted to Hertz as f_Q

$$f_Q = 3\omega_Q/2\pi = \frac{3e^2qQ}{h2I(2I-1)}. \quad (45)$$

Frequently, also half that value is used ($f'_Q = (3e^2qQ)/h4I(2I-1)$) [13,14]. For a spin 1, f'_Q then corresponds to the distance between the peaks in a Pake doublet when $\eta=0$.

3.2. Nuclear quadrupole resonance

Without the application of an external magnetic field, the Hamiltonian of Eq. (44) creates a discrete spectrum, a mode of operation that is commonly termed Nuclear Quadrupole Resonance (NQR) [15]. In particular, for $\eta=0$ one finds $2I$ resonance lines for a spin I , spaced by $3\omega_Q/(2\pi)$, centered at zero frequency. Slight differences are found for $\eta \neq 0$. This is observed regardless of the orientation of the system with respect to the measuring apparatus. The orientation merely has an influence on the relative intensities of the resonance lines.

The same is true for field-cycling experiments, where the zero-field quadrupolar frequencies are observed indirectly in a two-dimensional experiment. The spin-system is first polarized in a high magnetic field, then the system evolves at zero magnetic field and is finally observed again at a high magnetic field [16–18]. The orientation of the sample with respect to the polarizing magnetic field solely influences the relative intensities of the discrete resonance lines.

3.3. High magnetic fields and truncation

If the system is placed in a strong magnetic field such that the Zeeman interaction can be assumed to be much stronger than the quadrupolar interaction, the truncated version of Eq. (44) can be used, i.e.

$$H_Q = \omega_Q R_{2,0} T_{2,0} = \omega_Q R_{2,0} \frac{1}{\sqrt{6}} [3I_z^2 - I(I+1)]. \quad (46)$$

which represents the portion of the Hamiltonian that commutes with the Zeeman interaction (the same equation is applicable to NQR in the case of axial symmetry). Since in this case, a preferred axis of quantization is set by the Zeeman interaction through the orientation of the external magnetic field, we have to take into account the orientation of the principal axis frame of the R tensor with respect to

the magnetic field direction, i.e.

$$R_{2,0} = \sqrt{3/2} [P_2(\cos \beta) + (\eta/2) \cos 2\alpha \sin^2 \beta], \quad (47)$$

where α and β are two of the three Euler angles. If a sample is investigated that contains crystals with random distribution of orientations, a so-called powder spectrum is observed, such as those represented in Fig. 1.

A similar type of truncation may be obtained in NQR if one attempts to rotate the sample rapidly around an axis in the absence of an external magnetic field. Since the tensor components $R_{2,m}$ for $m \neq 0$ oscillate rapidly and average out over time, it appears as though the rotation axis imposes a quantization direction onto the spin-system. Eqs. (46) and (47) then apply as well, with the angles α and β determining the rotation from the principal axis system onto the rotating coordinate system. As a result, a powder lineshape is obtained. Frequently, however, the mechanical reorientation is not rapid enough and a series of discrete resonance lines arises.

By the same token, the case of rapid sample spinning in a high magnetic field can be considered as a ‘double truncation’, whereby the quadrupolar interaction is first quantized along the direction of the Zeeman Hamiltonian, resulting in a powder lineshape, and then along the direction of the rotor axis. The spatial part $R_{2,m}$ for $m \neq 0$ oscillates rapidly, and if the rotor axis is inclined at the magic angle with respect to the magnetic field (magic-angle spinning—MAS) the spatial portion $R_{2,0}$ is exactly zero. The case of double rotation (DOR) [19] may then be regarded as a triple truncation. Due to practical limitations, the truncation imposed by sample spinning is seldom complete and a series of spinning sidebands occurs.

If the Zeeman interaction is not overwhelmingly stronger than the quadrupolar interaction, higher terms in a perturbation series need to be considered. If the two interactions are of comparable strengths then the full Hamiltonian needs to be diagonalized and direct computer simulations may be the only applicable method for obtaining representations of NMR spectra [20]. A discussion on the transition from the NQR situation to the high-field NMR case can be found in Ref. [21].

In the following, we restrict ourselves to the case of a strong Zeeman interaction and we will only consider the first few terms in a perturbation expansion.

3.4. Higher order terms of H_Q perturbing the Zeeman Hamiltonian

The second-order quadrupolar interaction can be calculated from the second-order perturbation series for the non-degenerate case (the degenerate case would be found in NQR, which is irrelevant here)

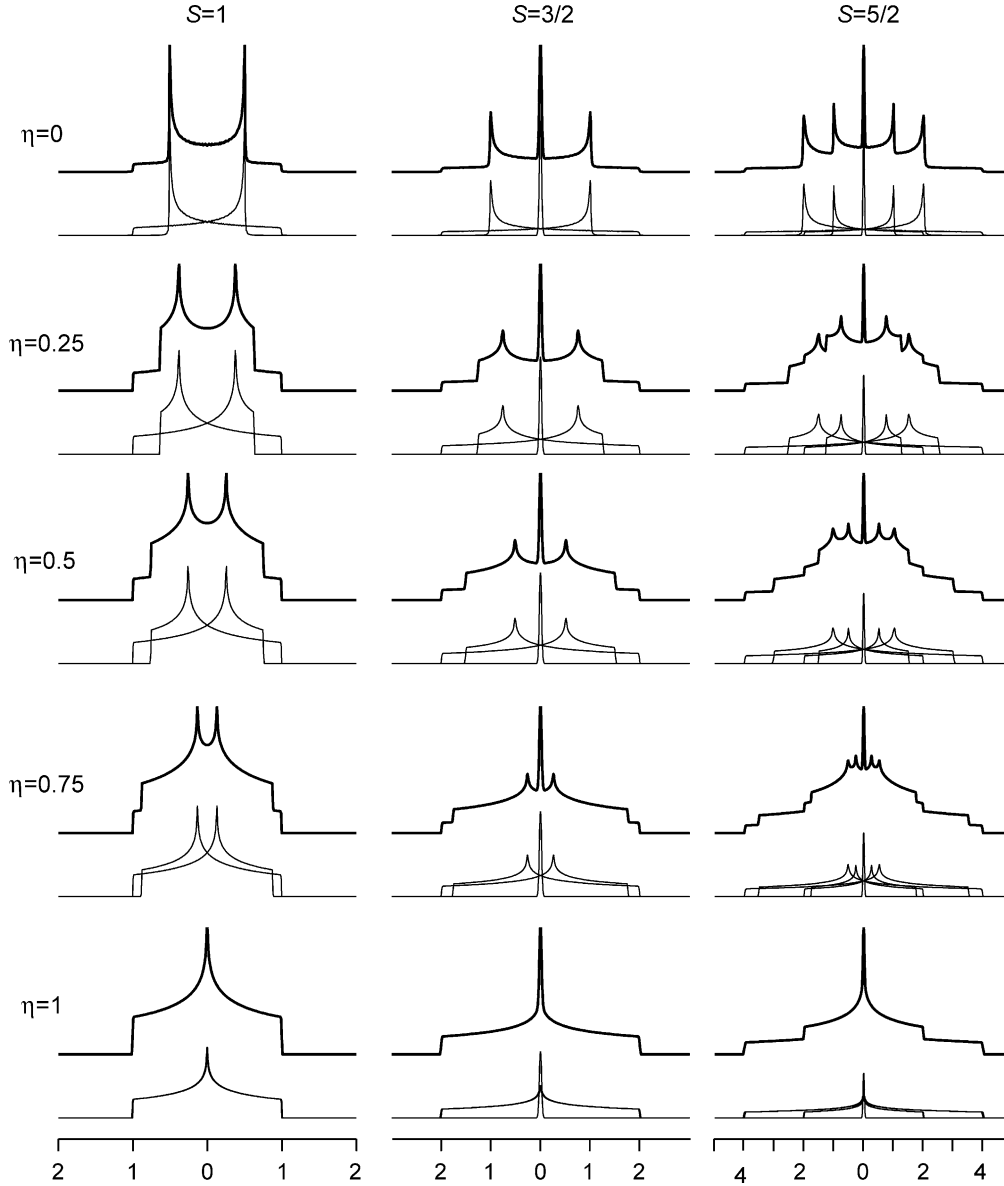


Fig. 1. First-order quadrupolar lineshapes in the high-field limit. The frequencies are plotted in units of $3\omega_Q/2\pi$. The lineshapes of the individual transitions are plotted underneath the overall powder spectrum.

$$\begin{aligned}
 E_j^{(2)} &= \frac{1}{\omega_0} \sum_{j \neq k} \frac{\langle j | H_Q | k \rangle \langle k | H_Q | j \rangle}{k - j} \\
 &= -\frac{\omega_Q^2}{\omega_0} \sum_{m \neq 0} \frac{R_{2,-m} R_{2,m} \langle j | T_{2,m} T_{2,-m} | j \rangle}{m}
 \end{aligned} \quad (48)$$

Splitting the sum over m into two equal parts and regrouping terms of opposite m into commutators, we get

$$H_Q^{(2)} = \frac{\omega_Q^2}{\omega_0} \sum_{m > 0} \frac{R_{2,-m} R_{2,m} [T_{2,-m}, T_{2,m}]}{m}, \quad (49)$$

When one attempts to derive the second-order term by Average Hamiltonian Theory, one obtains an additional term proportional to $[T_{2,m}, T_{2,0}]$, which can be shown to be

an artifact of the method. These issues were discussed extensively in [22–24].

The third-order contribution, which appears to be important in some experiments [25,26] can be derived from

$$H^{(3)} = \frac{1}{\omega_0^2} \sum_{k \neq 0, m \neq 0} \frac{1}{km} [H_{-k}, [H_{k-m}, H_m]], \quad (50)$$

where H_m is the portion of the Hamiltonian whose spin part transforms like an m -rank tensor.

Using

$$K_1 = [T_{2,-1}, T_{2,1}] = \frac{1}{2} I_z [4I(I+1) - 8I_z^2 - 1], \quad (51)$$

$$K_2 = [T_{2,-2}, T_{2,2}] = I_z [2I(I+1) - 2I_z^2 - 1]$$

we rewrite Eq. (49) as

$$H_Q^{(2)} = \frac{\omega_Q^2}{\omega_0} \left(R_{2,1}R_{2,-1}K_1 + \frac{1}{2}R_{2,2}R_{2,-2}K_2 \right) \quad (52)$$

Converting the products $R_{2,m}R_{2,-m}$ to the coupled representation $A_{l,m}$ we get

$$H_Q^{(2)} = \frac{\omega_Q^2}{\omega_0} \sum_{m=1} \sum_{2l=0,2,4} \frac{1}{m} A_{l,0} K_m \langle 2, -m; 2, m | l, 0 \rangle \quad (53)$$

In the principal axis frame we have

$$\begin{aligned} A_{0,0} = \rho_{0,0} &= \frac{3 + \eta^2}{2\sqrt{5}}, & A_{2,0} = \rho_{2,0} &= \frac{-3 + \eta^2}{\sqrt{14}}, \\ A_{4,0} = \rho_{4,0} &= \frac{18 + \eta^2}{2\sqrt{70}}. \end{aligned} \quad (54)$$

Evaluating the sum over m we obtain

$$\begin{aligned} H_Q^{(2)} = \frac{\omega_Q^2}{\omega_0} \left\{ \frac{1}{\sqrt{5}} A_{0,0} I_z [3I_z^2 - I(I+1)] \right. \\ \left. + \frac{1}{2\sqrt{14}} A_{2,0} I_z [8I(I+1) - 12I_z^2 - 3] \right. \\ \left. + \frac{1}{2\sqrt{70}} A_{4,0} I_z [18I(I+1) - 34I_z^2 - 5] \right\} \quad (55) \end{aligned}$$

The term containing $A_{0,0}$ transforms as a zero rank tensor, hence is independent of orientation and produces an isotropic shift, called the quadrupolar isotropic shift ω_{QIS} in radians or in Hertz. Using Eqs. (54) and (55) gives the shift as

$$\frac{C_Q^2(3 + \eta^2)I_z[3I_z^2 - I(I+1)]}{10\nu_0[2I(2I-1)]^2}. \quad (56)$$

in units of Hertz. For central transitions (from $-m$ to m) we may substitute $I_z = p/2$, where p is the coherence order, and considering that a transition frequency will be twice the energy shift we arrive at a frequently used expression for the quadrupolar isotropic shift ν_{QIS}

$$\nu_{QIS} = \frac{C_Q^2(3 + \eta^2)p[(3/4)p^2 - I(I+1)]}{10\nu_0[2I(2I-1)]^2}. \quad (57)$$

3.5. Rapid sample spinning

The second and fourth rank tensors $A_{l,0}$ display orientational dependence. In order to obtain the appropriate interaction in the laboratory reference frame one needs to perform rotations from their principal axis frame. It is customary to perform two Wigner rotations: One from the principal axis frame of the electric field gradient tensor into the frame of the rotor (including the current rotor angle), and from there to the laboratory frame. The sequence of rotations can be represented by

$$\begin{aligned} A_{l,0}(t) &= \sum_m \sum_n D_{m0}^l(\omega_r t, \theta, 0) D_{nm}^l(\alpha, \beta, \gamma) \rho_{l,n} \\ &= \sum_m \sum_n D_{m0}^l(0, \theta, 0) D_{nm}^l(\alpha, \beta, \gamma + \omega_r t) \rho_{l,n} \\ &= \sum_m \sum_n d_{m0}^l(\theta) d_{nm}^l(\beta) \exp(-in\alpha - im[\gamma + \omega_r t]) \rho_{l,n} \end{aligned} \quad (58)$$

where α, β, γ are the three Euler angles to rotate the tensor from the principal axis frame into the rotor frame, θ is the angle between the static magnetic field and the rotor axis, and ω_r is the rotor speed. The non-zero tensors in the coupled representation in the principal axis frame are

$$\begin{aligned} \rho_{0,0} &= \frac{3 + \eta^2}{2\sqrt{5}}, & \rho_{2,0} &= \frac{-3 + \eta^2}{\sqrt{14}}, \\ \rho_{2,\pm 2} &= \eta\sqrt{\frac{3}{7}}, & \rho_{4,0} &= \frac{18 + \eta^2}{2\sqrt{70}}, \\ \rho_{4,\pm 2} &= \frac{3\eta}{2\sqrt{7}}, & \rho_{4,\pm 4} &= \frac{\eta^2}{4}. \end{aligned} \quad (59)$$

For numerical calculations, it is often convenient to cast Eq. (58) in a form of the type

$$A_{l,0}(t) = c_{l,0} + \sum_{m>0} c_{l,m} \cos(m\gamma') + s_{l,m} \sin(m\gamma') \quad (60)$$

where $\gamma' = \gamma + \omega_r t$. The coefficients $c_{l,m}$ and $s_{l,m}$ are then determined as follows

$$c_{l,0} = d_{00}^l(\theta) \left[d_{00}^l(\beta) \rho_{l,0} + 2 \sum_{n=2,4} d_{n0}^l(\beta) \cos(n\alpha) \rho_{l,n} \right] \quad (61)$$

$$c_{l,m} = 2d_{m0}^l(\theta) \sum_{n=0,2,4} [d_{nm}^l(\beta) + (1 - \delta_{n0})d_{-nm}^l(\beta)] \rho_{l,n} \cos(n\alpha) \quad (62)$$

$$s_{l,m} = -2d_{m0}^l(\theta) \sum_{n=2,4} [d_{nm}^l(\beta) - d_{-nm}^l(\beta)] \rho_{l,n} \sin(n\alpha) \quad (63)$$

where we have used the Kronecker δ_{n0} . The explicit calculation of these terms is shown in Appendix A.

Under conditions of infinite spinning one can neglect the $c_{l,0}$ term. If one is not interested in studying the spinning sidebands in detail, this is a fairly reliable approach.

Eqs. (61)–(63) and their specific forms given in Appendix A become increasingly complicated if one studies cases where several interactions are present with different principal axis frames. These can couple in second or higher orders (e.g. second-order dipolar/quadrupolar couplings [27], or second-order CSA–quadrupolar terms [28]). In these situations, it is probably more straightforward to perform the simulation in the uncoupled representation. For considerations of computational speed, one may still invoke the infinite spinning assumption if one

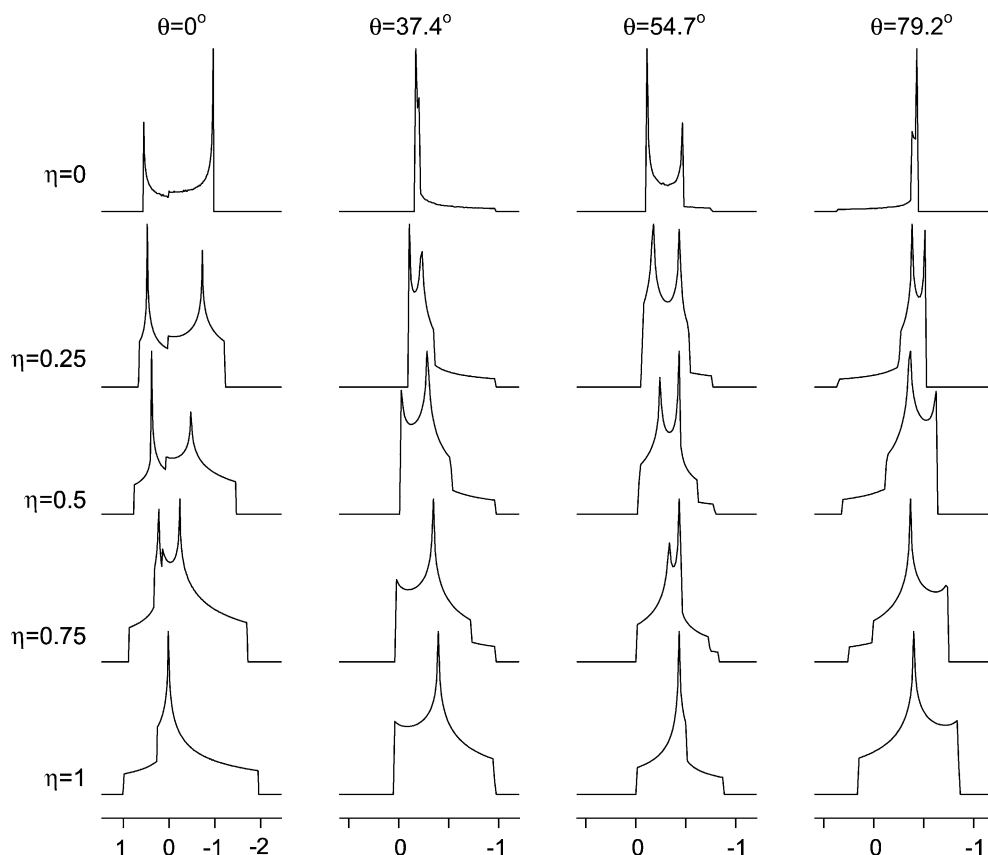


Fig. 2. Second-order quadrupolar lineshapes for different spinning angles and anisotropies. The frequencies are displayed in units of $(\omega_Q^2/2\pi\omega_0)[I(I+1) - 3/4]$.

combines only tensors with opposite order in the rotor axis frame.

The coupled representation is nevertheless quite useful for general discussions and for the study of the underlying symmetries [29–31].

If the spinning angle is $\theta = 54.74^\circ$ then Eq. (61) together with the infinite spinning assumption predicts that the only residual term left is $c_{4,0}$.

Exact expressions for the MAS frequency spectra obtained from quadrupolar nuclei under both the first- and second-order quadrupole couplings have been given elsewhere [32]. The terms $c_{l,m}$ and $s_{l,m}$ can be used to derive the intensities of spinning sidebands in a variety of experiments [33,34]. Fig. 2 shows the powder lineshapes obtained under static and spinning conditions at different θ angles.

3.6. Nutation spectroscopy

A very useful method for determining quadrupolar coupling constants is the nutation experiment [35]. In this two-dimensional experiment, one applies a long rf irradiation either to the spin system in equilibrium, or to the spins after preparation by a soft pulse, followed by the acquisition of a free induction decay. The duration of the rf irradiation is incremented and represents the time variable t_1

for the indirect dimension of the two-dimensional experiment. After Fourier transformation, the spectra show correlations between the peaks of the central transitions (the method is mostly applied to half-integer spins), and peaks located at the nutation frequencies in the indirect frequency dimension. Quadrupolar couplings and anisotropy parameters can be determined by comparing these nutation spectra to computer simulations.

The method draws on the fact that applying rf irradiation with power ω_{rf} leads to a nutation speed of the magnetization components which depends sensitively on the ratio ω_{rf}/ω_Q . The extreme cases are when $\omega_{rf} \ll \omega_Q$, for which the nutation frequency is equal to $\omega_{rf}(I + 1/2)$, and $\omega_{rf} \ll \omega_Q$, when it is ω_{rf} . In powder samples, the experimental spectra show sufficient structure to be fitted with appropriate simulations [35]. Nutation spectroscopy appears most powerful in cases with very large quadrupolar coupling constants where methods such as MQMAS may not be applicable.

3.7. Overtone spectroscopy

If the quadrupolar coupling constant is large such that ω_Q is no longer negligibly small compared to ω_0 , higher orders of perturbation need to be taken into account. The z -axis is

no longer a good quantization axis. The corrections to the eigenvectors are calculated to first order as [22]

$$|j^{(1)}\rangle = -\frac{\omega_Q}{\omega_0} \sum_{m \neq 0} (-1)^m \frac{R_{2,-m} T_{2,m}}{m} |j\rangle. \quad (64)$$

To order ω_Q/ω_0 the transition moments of the operators I_+ , and I_z are then non-zero for $\Delta j=0,2,3$ and $\Delta j=1,2$, respectively (neglecting those cases where negative Larmor frequencies would occur). Therefore, one may excite and detect transitions at twice and triple the Larmor frequency by transverse rf-fields, and at the Larmor frequency and twice that frequency by rf-fields collinear with the static magnetic field. Higher order terms in the perturbation will give resonances at higher multiples of the Larmor frequency but with lower signal intensity.

Overtone spectroscopy is especially interesting for studying ^{14}N , where by observing the $m = -1$ to $+1$ transition at ω_0 one obtains spectra devoid of first-order quadrupolar broadening [36–38]. This was exploited for a number of applications, including cross-polarization, separated-local field measurements [36–38], overtone-nutation spectra [39], and heteronuclear recoupling [40]. The effect of spinning on the appearance of overtone spectra has been analyzed by Takegoshi and Hikichi [41]. Recently, a set of overtone transitions was observed for ^{35}Cl in a single crystal [42].

4. High-resolution spectroscopy of quadrupolar nuclei

4.1. Double rotation—DOR

Even if it were possible to rotate a powder sample at infinite speeds, one would not succeed in eliminating the additional linebroadening originating in the second and higher orders of perturbation. In the limit where the second-order perturbation term is sufficient, the terms $A_{2,0} = c_{2,0}$ and $A_{4,0} = c_{4,0}$ of Eq. (61) determine the orientational dependence of the resonance frequencies. As there is no spinning angle θ at which both the factors $d_{00}^2(\theta) = P_2(\cos \theta)$ and $d_{00}^4(\theta) = P_4(\cos \theta)$ can be made zero at the same time a residual broadening remains, whatever the value of θ .

In the Double Rotation experiment (DOR) [19], the sample is spun at two different angles in a rotor-in-a-rotor design. One can formally write down the orientational and spinning dependence in a way similar to Eq. (58) as

$$\begin{aligned} A_{l,0}(t) &= \sum_m \sum_n \sum_p D_{p0}^l(\omega_r^{(2)} t, \theta^{(2)}, 0) D_{mp}^l \\ &\quad (\omega_r^{(1)} t, \theta^{(1)}, \phi) D_{nm}^l(\alpha, \beta, \gamma) \rho_{l,n} \\ &= \sum_{mpn} d_{m0}^l(\theta^{(2)}) d_{mp}^l(\theta^{(1)}) d_{nm}^l(\beta) \exp[-i n \alpha - i m \gamma] \end{aligned} \quad (65)$$

where $\theta^{(1)}$, $\omega_r^{(1)}$, and $\theta^{(2)}$, $\omega_r^{(2)}$ define the parameters of the first and the second spinning axes, and ϕ is the relative spinning angle between the first rotor and the second rotor at the start of the experiment. Under conditions of infinite

spinning speed the only remaining term is

$$A_{l,0} = \sum_{mpn} d_{00}^l(\theta^{(2)}) d_{00}^l(\theta^{(1)}) d_{n0}^l(\beta) \exp[-i n \alpha] \rho_{l,n}. \quad (66)$$

If the spinning axes are chosen such that both $d_{00}^2(\theta^{(1)}) = 0$ and $d_{00}^4(\theta^{(2)}) = 0$, then no additional broadening arises and a high-resolution spectrum may be obtained (e.g. when $\theta^{(1)} = 54.74^\circ$ and $\theta^{(2)} = 30.56^\circ$).

In the experimental implementations, the spinning speeds $\omega_r^{(1)}$ and $\omega_r^{(2)}$ are much smaller than ω_Q and a large number of spinning sidebands appears. Nevertheless, the individual sidebands and the centerband can be obtained in sufficiently high resolution such that different crystallographic sites may be distinguished. The sideband patterns and intensities were given by Sun et al. [43]

4.2. Dynamic-angle spinning—DAS

A mechanically much less demanding approach is to spin at two different angles sequentially rather than simultaneously [44,45]. One can find two different spinning angles $\theta^{(1)}$ and $\theta^{(2)}$ and constants a and b such that

$$\begin{aligned} a d_{00}^2(\theta^{(1)}) &= -b d_{00}^2(\theta^{(1)}), \\ a d_{00}^4(\theta^{(2)}) &= -b d_{00}^4(\theta^{(2)}), \quad a + b = 1. \end{aligned} \quad (67)$$

One can then perform a partial echo of the residual quadrupolar interaction during the t_1 period of a two-dimensional experiment as illustrated in Fig. 3. This is done by spinning in one period ($a \times t_1$) at an angle $\theta^{(1)}$ and during the other, ($b \times t_1$), at $\theta^{(2)}$. When $a = b = 1/2$ there is only one such solution, $\theta^{(1)} = 37.4^\circ$ and $\theta^{(2)} = 79.2^\circ$. Fig. 2 shows the powder spectra due to second-order broadening at both these spinning angles. The patterns at $\theta^{(1)} = 37.4^\circ$ and $\theta^{(2)} = 79.2^\circ$ are exact mirror images of each other, which highlights the fact that a partial echo can be performed to refocus the residual broadening.

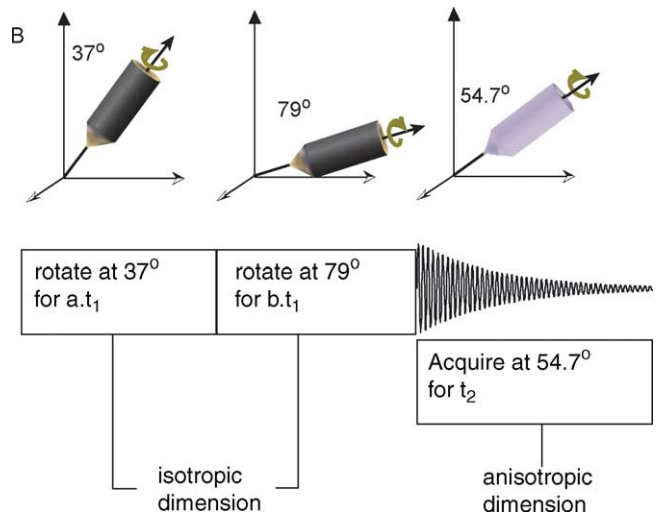


Fig. 3. Dynamic-angle spinning experiment.

When $a \neq b$ many more such combinations can be found. When the spinning speed is finite, sidebands form [43,46,47].

In principle, pulses are not required between the two t_1 periods. In practice, the switching time between the two spinning angles is relatively long (of the order of 50 ms) and the magnetization is usually stored along the z direction and subsequently brought back to the transverse plane. Any other interactions of rank two or four will also be eliminated in this way.

While in many areas this experiment has been superseded by MQMAS, it should be noted that, it is currently the only high-resolution method applicable to integer spins.

4.3. Multiple-quantum MAS—MQMAS

When spinning at the magic angle, the only term responsible for the residual broadening is

$$A_{4,0}I_z[18I(I+1) - 34I_z^2 - 5]. \quad (68)$$

The orientational dependence is determined by the spatial part $A_{4,0}$, whereas the spin part $I_z[18I(I+1) - 34I_z^2 - 5]$ leads to scaling of the powder lineshape. The MQMAS experiment uses a combination of two different spin transitions in order to refocus the evolution based on this second-order term. The t_1 period is divided into two, of durations at_1 and bt_1 , with $a+b=1$, as illustrated in Fig. 4 [48,49].

Usually, odd multiple-quantum coherence is created first, and is then converted to single-quantum coherence. No first-order broadenings appear for symmetric transitions. Furthermore, the scaling factor relating the powder lineshape of the multiple-quantum coherence to the one of

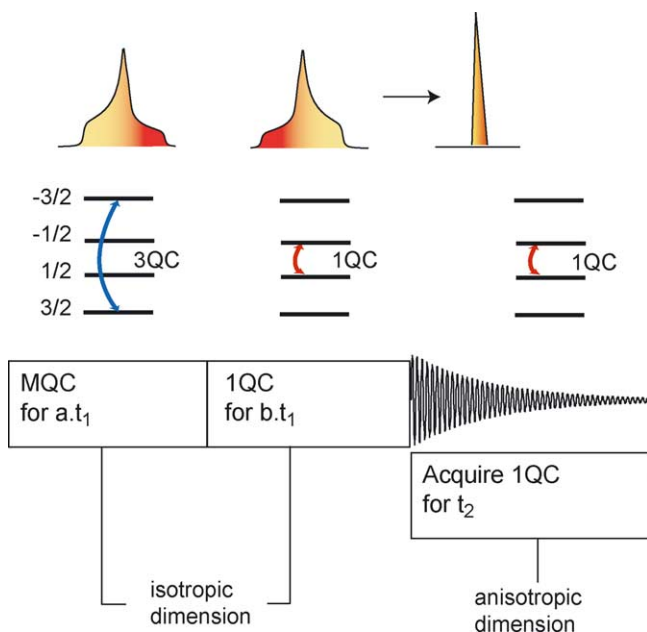


Fig. 4. Multiple-quantum magic-angle spinning experiment.

the single-quantum coherence should be negative to insure the formation of an echo. If it is positive, the coherence order with opposite sign has to be used. In a more general approach one may use two different multiple-quantum coherences during the t_1 period in order to form the echo [50].

The timings of the two periods at_1 and bt_1 are adjusted such that

$$a = C_0^4(p_2)/[C_0^4(p_1) + C_0^4(p_2)], \quad (69)$$

$$b = C_0^4(p_1)/[C_0^4(p_1) + C_0^4(p_2)]$$

where $C_0^4(p)$ represents the spin-dependent part of the fourth-rank term responsible for the broadening, defined in analogy to Eq. (68) as

$$C_0^4(p) = (p/2) \left[18I(I+1) - \frac{17}{2}p^2 - 5 \right]. \quad (70)$$

p_1 and p_2 are the two different multiple-quantum or single-quantum coherence orders used during the t_1 -period. Table 1 summarizes the factors a and b to be used for a number of spin values and coherence order combinations.

Table 1

$P_Q^2 = C_Q^2(1 + \eta^2/3)$, in MHz^2 , ν_0 is given in MHz, δ_1 , δ_2 , δ_{CS} in ppm

	p_1	p_2	a	b	δ_{CS}	P_Q^2
$S=3/2$	3	1	$\frac{9}{16}$	$\frac{7}{16}$	$\frac{2(4\delta_1+5\delta_2)}{27}$	$\frac{(8\delta_1-17\delta_2)\nu_0^2}{675000}$
$S=5/2$	3	-1	$\frac{12}{31}$	$\frac{19}{31}$	$\frac{31\delta_1+10\delta_2}{27}$	$\frac{(31\delta_1-17\delta_2)\nu_0^2}{162000}$
	5	1	$\frac{12}{37}$	$\frac{25}{37}$	$\frac{37\delta_1+50\delta_2}{135}$	$\frac{(37\delta_1-85\delta_2)\nu_0^2}{810000}$
	5	3	$\frac{19}{44}$	$\frac{25}{44}$	$\frac{2(11\delta_1+25\delta_2)}{135}$	$\frac{(22\delta_1-85\delta_2)\nu_0^2}{810000}$
$S=7/2$	3	-1	$\frac{45}{146}$	$\frac{101}{146}$	$\frac{73\delta_1+10\delta_2}{27}$	$\frac{49(73\delta_1-17\delta_2)\nu_0^2}{3375000}$
	5	-1	$\frac{9}{20}$	$\frac{11}{20}$	$\frac{10(\delta_1+\delta_2)}{27}$	$\frac{49(10\delta_1-17\delta_2)\nu_0^2}{3375000}$
	5	-3	$\frac{101}{156}$	$\frac{55}{156}$	$\frac{39\delta_1+50\delta_2}{135}$	$\frac{49(39\delta_1-85\delta_2)\nu_0^2}{16875000}$
	7	1	$\frac{45}{206}$	$\frac{161}{206}$	$\frac{103\delta_1+140\delta_2}{378}$	$\frac{7(103\delta_1-238\delta_2)\nu_0^2}{6750000}$
	7	3	$\frac{101}{262}$	$\frac{161}{262}$	$\frac{131\delta_1+140\delta_2}{945}$	$\frac{7(131\delta_1-595\delta_2)\nu_0^2}{16875000}$
	7	5	$\frac{55}{216}$	$\frac{161}{216}$	$\frac{2(54\delta_1+175\delta_2)}{945}$	$\frac{7(108\delta_1-595\delta_2)\nu_0^2}{16875000}$
$S=9/2$	3	-1	$\frac{36}{127}$	$\frac{91}{127}$	$\frac{127\delta_1+10\delta_2}{27}$	$\frac{(127\delta_1-17\delta_2)\nu_0^2}{37500}$
	5	-1	$\frac{36}{131}$	$\frac{95}{131}$	$\frac{131\delta_1+50\delta_2}{135}$	$\frac{(131\delta_1-85\delta_2)\nu_0^2}{187500}$
	5	-3	$\frac{91}{186}$	$\frac{95}{186}$	$\frac{93\delta_1+50\delta_2}{135}$	$\frac{(93\delta_1-85\delta_2)\nu_0^2}{187500}$
	7	-1	$\frac{18}{25}$	$\frac{7}{25}$	$\frac{5(5\delta_1+14\delta_2)}{189}$	$\frac{(25\delta_1-119\delta_2)\nu_0^2}{262500}$
	7	-3	$\frac{13}{15}$	$\frac{2}{15}$	$\frac{3\delta_1+10\delta_2}{27}$	$\frac{(3\delta_1-17\delta_2)\nu_0^2}{1312500}$
	7	-5	$\frac{95}{109}$	$\frac{14}{109}$	$\frac{109\delta_1+350\delta_2}{945}$	$\frac{(109\delta_1-595\delta_2)\nu_0^2}{1312500}$
	9	1	$\frac{6}{37}$	$\frac{31}{37}$	$\frac{37\delta_1+50\delta_2}{135}$	$\frac{(37\delta_1-85\delta_2)\nu_0^2}{187500}$
	9	3	$\frac{91}{277}$	$\frac{186}{277}$	$\frac{277\delta_1+810\delta_2}{2187}$	$\frac{(277\delta_1-1377\delta_2)\nu_0^2}{3037500}$
	9	5	$\frac{95}{281}$	$\frac{186}{281}$	$\frac{281\delta_1+1050\delta_2}{2835}$	$\frac{(281\delta_1-1785\delta_2)\nu_0^2}{3937500}$
	9	7	$\frac{7}{100}$	$\frac{93}{100}$	$\frac{10(5\delta_1+21\delta_2)}{567}$	$\frac{(50\delta_1-357\delta_2)\nu_0^2}{787500}$

The two columns to the right show how the chemical shifts and the quadrupolar coupling constant (in the form of P_Q) can be extracted using the center-of-gravity peak positions in a MQMAS experiment.

There exist a number of variants of the basic two-pulse MQMAS experiment [48,49], including the z -filter [51], the shifted-echo [52], and an experiment that uses several different coherence pathways simultaneously [53]. Sensitivity improvements in the coherence transfers have been achieved by applying fast amplitude-modulated pulses [54–59], double-frequency sweeps [60–63], or taking advantage of rotational resonance effects [64–74]. The use of a CPMG-pulse train can yield a substantial signal enhancement [75–77].

The MQMAS experiment is now a widely popular technique for obtaining high-resolution spectra of quadrupolar nuclei in solids, since it allows one to use routine hardware components without special modifications.

The representations of the spectra are often produced using different conventions for labeling the ppm axis in the isotropic dimension. Two frequent procedures are: (1) the frequencies in $F1$ are divided by the Larmor frequency of the observed nucleus—this is probably the most natural convention; (2) the frequencies in $F1$ are divided by the Larmor frequency times the chemical shift scaling factor, so that on a ppm-scale chemical shifts stay the same whatever the multiple-quantum coherence order used [78,79]. The latter appears inconvenient since quadrupolar isotropic shifts lead to different peak positions at different magnetic fields and need to be corrected for this additional scaling factor. Some other conventions are based on the use of only the first multiple-quantum period as the ‘actual t_1 -period’, i.e. at_1 . In this case, the axis needs to be multiplied by the factor a to obtain the original ppm-scale. Other conventions may require one to change the sign of the $F1$ -axis labeling [78,79]. A discussion of different conventions can be found in Refs. [14,78,79].

We feel that adoption of convention (1), and assuming an experiment of the type displayed in Fig. 4, where $a+b=1$, is a convenient choice. This procedure is also the recommended one in a recent review article [14].

One can use the center of gravity peak positions in a MQMAS experiment to determine the chemical shifts and quadrupole coupling constants for the individual resonances as follows.

The evolution frequency (in ppm) of p -quantum coherence is given by

$$\delta(p) = -[\delta_{\text{CS}}p + \nu_{\text{QIS}}(p)/\nu_0], \quad (71)$$

where δ_{CS} is the chemical shift in ppm, and $\nu_{\text{QIS}}(p)$ is given by Eq. (57). The positions of the peaks in $F1$ and $F2$ are then given by

$$\delta_1 = a\delta(p_1) + b\delta(p_2), \quad \delta_2 = \delta(-1). \quad (72)$$

Given the position of the center of gravity of a resonance in a two-dimensional MQMAS spectrum one may extract the chemical shifts and the quadrupolar coupling parameter $P_Q = C_Q\sqrt{1+\eta^2/3}$ by inverting Eq. (72). These expressions are shown in Table 1 for a number of relevant

cases. In line with common practice in the NMR literature, the resonance frequencies of positive coherence orders during the t_1 interval are inverted in sign. The η parameters can often be extracted by fitting the lineshapes of the resonances along the $F2$ dimension.

A number of review articles describe MQMAS and STMAS experiments and their applications in more detail [14,80–87].

4.4. Satellite transition MAS—STMAS

It is also possible to obtain high-resolution spectra by correlating a satellite transition with the central transition of a half-integer nucleus [88,89]. The experiment requires very accurate rotor synchronization and setting of the magic angle [90]. The appearance of the first-order quadrupolar interaction is avoided by assuring exact rotor synchronization during the t_1 -period, which makes all spinning sidebands overlap on top of each other. Recently, a pulse sequence has been described, that allows one to reduce the sensitivity to magic-angle offsets [91,92]. One may also use double-quantum transitions which involve satellite transitions during the t_1 evolution delay [91]. Double-quantum filtration can further be used to avoid the appearance of a number of unwanted signals [93] in STMAS experiments. Proper a and b parameters for these types of experiments may be derived from Eq. (68).

STMAS experiments are in general subject to odd-order broadening [25], broadening due to motion, and inaccuracies related to magic-angle missetting [94], which are normally absent or less problematic for central-transition MQMAS experiments. For further details, we wish to point the reader to the comprehensive review by Ashbrook and Wimperis [14].

STMAS may further be applicable to any spins larger than one, whether it is an integer spin or a half-integer spin. For spin one nuclei such a procedure is not helpful because it is impossible to find a combination of transitions that affords a partial echo for the second-order quadrupolar interaction that does not at the same time refocus the isotropic chemical shifts.

4.5. Other experiments

MQMAS experiments have been combined with cross-polarization (CP) to single quantum or to multiple-quantum coherences. Heteronuclear correlation experiments between two quadrupolar nuclei, or between a quadrupolar nucleus and a spin 1/2 nucleus have been performed [95–106]. Recoupling schemes have been investigated [107–110]. Some homonuclear quadrupolar correlation experiments have been documented [111–114], as well as exchange experiments [115], and J -resolved experiments [116].

5. Conclusions

Very advanced techniques for the study of quadrupolar nuclei are available, and the theoretical description of these experiments is well established. The existence of a number of different definitions for the quadrupolar interactions frequently leads to confusion in comparing work from different sources. In this review article, the author has attempted to establish a link between nuclear structure constants and the NMR Hamiltonian and the spectra obtained by NMR methods. It is hoped that the article will provide a useful reference point for describing the quadrupolar interaction, but also to facilitate the interface between NMR and nuclear physics literature.

Acknowledgements

The author wishes to express his gratitude for very insightful and stimulating discussions with S. Vega, C.P. Slichter, S. Wimperis, P.K. Madhu, G. Denninger, and S.C. Shekar. This work also benefitted from infrastructure provided through a National Science Foundation Grant, ‘Research Coordination Network for NMR of Biological Solids’ (MCB-0233854). The author is a member of the New York Structural Biology Center supported by NIH Grant 1P41GM66354 and the Center’s Metagroup Meetings are acknowledged for helpful discussions.

Appendix A

A.1. Other second-order interactions

A.1.1. Quadrupolar/dipolar coupling

The second-order cross-term between the quadrupolar coupling and the dipolar coupling can be determined from equations similar to Eqs. (48) and (49). For the heteronuclear case one obtains [27]

$$H_{Q,DD}^{(2)} = -\frac{\omega_Q^I \omega_{D,eff}}{2\omega_0^I} (R_{2,-1}^{Q,I} R_{2,1}^{D,eff} + R_{2,1}^{Q,I} R_{2,-1}^{D,eff}) \times [3I_z^2 - I(I+1)]S_z - \frac{\omega_Q^S \omega_{D,eff}}{2\omega_0^S} (R_{2,-1}^{Q,S} R_{2,1}^{D,eff} + R_{2,1}^{Q,S} R_{2,-1}^{D,eff}) [3S_z^2 - S(S+1)]I_z \quad (A1)$$

where

$$\omega_{D,eff} = -\frac{\mu_0 \hbar \gamma_I \gamma_S}{4\pi r_{IS}^3} + J_{aniso}^{IS} \quad (A2)$$

and $R_{2,0}^{D,eff} = \sqrt{6}$ in the principal axis frame. $R_{l,m}^{Q,S}$ and $R_{l,m}^{Q,I}$ as well as, ω_Q^S and ω_Q^I are the quadrupolar tensors and constants for spin S and I , respectively, and ω_0^S and ω_0^I their Larmor frequencies.

For the homonuclear case, one obtains [27]

$$H_{Q,DD}^{(2)} = -\frac{\omega_Q^I \omega_{D,eff}}{2\omega_0^I} (R_{2,-1}^{Q,I} R_{2,1}^{D,eff} + R_{2,1}^{Q,I} R_{2,-1}^{D,eff}) \times [3I_z^2 - I(I+1)]S_z - \frac{\omega_Q^S \omega_{D,eff}}{2\omega_0^S} (R_{2,-1}^{Q,S} R_{2,1}^{D,eff} + R_{2,1}^{Q,S} R_{2,-1}^{D,eff}) [3S_z^2 - S(S+1)]I_z + \frac{\omega_Q^S \omega_{D,eff}}{4\omega_0^S} (R_{2,-1}^{Q,S} R_{2,1}^{D,eff} + R_{2,-2}^{Q,S} R_{2,2}^{D,eff}) \times S_+ I_- (2S_z + 1) + \frac{\omega_Q^I \omega_{D,eff}}{4\omega_0^I} (R_{2,-1}^{Q,I} R_{2,1}^{D,eff} + R_{2,-2}^{Q,I} R_{2,2}^{D,eff}) S_- I_+ (2I_z + 1) + \frac{\omega_Q^S \omega_{D,eff}}{4\omega_0^S} (R_{2,1}^{Q,S} R_{2,-1}^{D,eff} + R_{2,2}^{Q,S} R_{2,-2}^{D,eff}) S_- I_+ (2S_z - 1) + \frac{\omega_Q^I \omega_{D,eff}}{4\omega_0^I} (R_{2,1}^{Q,I} R_{2,-1}^{D,eff} + R_{2,2}^{Q,I} R_{2,-2}^{D,eff}) S_+ I_- (2I_z - 1). \quad (A3)$$

A.1.2. Quadrupolar/chemical shift

The second-order cross-term between the quadrupolar coupling and the chemical shift Hamiltonian can be determined from Eq. (48) to be [28]

$$H_{Q,CS}^{(2)} = -\frac{\omega_Q}{2} [(R_{2,1}^Q R_{2,-1}^{CS} + R_{2,-1}^Q R_{2,1}^{CS}) + (R_{2,1}^Q R_{1,-1}^{CS} + R_{2,-1}^Q R_{1,1}^{CS})] [3I_z^2 - I(I+1)], \quad (A4)$$

where the chemical shift spatial tensors are taken as $R_{lm}^{CS} = \sum_{m'} D_{m'l}(\alpha, \beta, \gamma) \rho_{lm}^{CS}$ with the non-zero components in the principal axis frame of

$$\rho_{10}^{CS} = -\sqrt{2}i\sigma_{XY}^a, \quad \rho_{1\pm 1}^{CS} = \sigma_{XZ}^a \pm i\sigma_{YZ}^a, \quad (A5)$$

$$\rho_{20}^{CS} = \sqrt{\frac{3}{2}}\sigma_{CSA}, \quad \rho_{2\pm 2}^{CS} = \eta_{CS}\sigma_{CSA}/2.$$

In Eq. (A4) the antisymmetric components involving $R_{1\pm 1}^{CS}$ can be shown to cancel if the average over a full rotation period is considered. As with all such second-order contributions, an overall frequency shift results from this cross-term.

Because the only level-dependent component in the spin part is I_z^2 , these effects are not visible when symmetric transitions are observed.

A.1.3. Additional cross-terms

It has further been shown that for quadrupolar couplings of the order of the spinning speed, i.e. $\omega_Q \approx \omega_r$ additional line-broadening mechanisms may occur. They stem from

the interplay between the non-commuting dipolar and quadrupolar coupling Hamiltonians during sample spinning [117]. These effects are similar to $n=0$ rotational resonance effects shown for the interplay between chemical shift anisotropy and dipolar terms. These mechanisms are only relevant for small quadrupolar coupling constants ($\omega_Q \approx 5\text{--}25$ kHz). The remarkable feature of these effects is the increase of the linewidth with an increasing spinning frequency and may be quite surprising when studying an everyday setup sample such as KBr.

A.2. Sine and cosine representation of the first- and second-order quadrupolar frequencies

A.2.1. First order

$$\begin{aligned} c_0 &= \sqrt{\frac{3}{2}} P_2(\cos \theta) (P_2(\cos \beta) + (\eta/2) \cos 2\alpha \sin^2 \beta), \\ c_1 &= \frac{\sqrt{3}}{4\sqrt{2}} (-3 + \eta \cos 2\alpha) \sin 2\beta \sin 2\theta, \\ c_2 &= \frac{\sqrt{3}}{8\sqrt{2}} (\eta \cos 2\alpha (3 + \cos 2\beta) + 6 \sin^2 \beta) \sin^2 \theta, \\ s_1 &= -\sqrt{\frac{3}{8}} \eta \sin \beta \sin 2\alpha \sin 2\theta, \\ s_2 &= -\sqrt{\frac{3}{8}} \eta \cos \beta \cos 2\alpha \sin^2 \theta \end{aligned} \quad (\text{A6})$$

A.2.2. Second order

$$\begin{aligned} c_{2,0} &= \frac{1}{\sqrt{14}} P_2(\cos \theta) [(-3 + \eta^2) P_2(\cos \beta) \\ &\quad + 3\eta \cos 2\alpha \sin^2 \beta] \\ c_{4,0} &= \frac{1}{128\sqrt{70}} P_4(\cos \theta) [162 + 9\eta^2 + 35(18 + \eta^2) \cos 4\beta \\ &\quad + 1200\eta \cos 2\alpha \sin^2 \beta + 280\eta^2 \cos 4\alpha \sin^4 \beta \\ &\quad + 20 \cos 2\beta (18 + \eta^2 + 84\eta \cos 2\alpha \sin^2 \beta)] \\ c_{2,1} &= \frac{3}{4\sqrt{14}} [3 - \eta^2 + 2\eta \cos 2\alpha] \sin 2\beta \sin 2\theta \\ c_{2,2} &= \frac{3}{4\sqrt{14}} [\eta(3 + \cos 2\beta) \cos 2\alpha + (-3 + \eta^2) \sin^2 \beta] \sin^2 \theta \end{aligned} \quad (\text{A7})$$

$$\begin{aligned} c_{4,1} &= -\frac{\sqrt{5}}{1024\sqrt{14}} (-56\eta^2 \cos \beta \cos 4\alpha \sin^3 \beta \\ &\quad + 2(18 + \eta^2 + 12\eta \cos 2\alpha) \sin 2\beta + 7(18 + \eta^2 \\ &\quad - 12\eta \cos 2\alpha) \sin 4\beta) (2 \sin 2\theta + 7 \sin 4\theta) \\ c_{4,2} &= -\frac{\sqrt{5}}{128\sqrt{14}} (5 + 7 \cos 2\theta) [3\eta(5 + 4 \cos 2\beta \\ &\quad + 7 \cos 4\beta) \cos 2\alpha + (90 + 5\eta^2 + 21\eta^2 \cos 4\alpha \\ &\quad + 7 \cos 2\beta (18 + \eta^2 + \eta^2 \cos 4\alpha)) \sin^2 \beta] \sin^2 \theta \\ c_{4,3} &= -\frac{\sqrt{35}}{128\sqrt{2}} \cos \theta [96\eta \cos^3 \beta \cos 2\alpha \sin \beta \\ &\quad + 8(18 + \eta^2) \cos \beta \sin^3 \beta - \eta^2 \cos 4\alpha (14 \sin 2\beta \\ &\quad + \sin 4\beta)] \sin^3 \theta \\ c_{4,4} &= \frac{\sqrt{35}}{1024\sqrt{2}} [\eta^2 (35 + 28 \cos 2\beta + \cos 4\beta) \cos 4\alpha \\ &\quad + 8 \sin^2 \beta (6\eta(3 + \cos 2\beta) \cos 2\alpha \\ &\quad + (18 + \eta^2) \sin^2 \beta)] \sin^4 \theta \\ s_{2,1} &= -\frac{3}{\sqrt{14}} \eta \sin \beta \sin 2\alpha \sin 2\theta \\ s_{2,2} &= \frac{-3}{\sqrt{14}} \eta \cos \beta \sin 2\alpha \sin^2 \theta \\ s_{4,1} &= -\frac{\sqrt{5}}{128\sqrt{14}} \eta \sin \beta [3(5 + 7 \cos 2\beta) \sin 2\alpha \\ &\quad + 7\eta \sin^2 \beta \sin 4\alpha] (2 \sin 2\theta + 7 \sin 4\theta) \\ s_{4,2} &= -\frac{\sqrt{5}}{64\sqrt{14}} \eta (5 + 7 \cos 2\theta) [3(\cos \beta + 7 \cos 3\beta) \sin 2\alpha \\ &\quad + 14\eta \cos \beta \sin^2 \beta \sin 4\alpha] \sin^2 \theta \\ s_{4,3} &= -\frac{\sqrt{35}}{32\sqrt{2}} \eta [-6 - 18 \cos 2\beta + 3\eta \cos(2\beta - 2\alpha) \\ &\quad + 10\eta \cos 2\alpha + 3\eta \cos(2\beta + 2\alpha) \\ &\quad \times \cos \theta \sin \beta \sin 2\alpha \sin^3 \theta] \\ s_{4,4} &= -\frac{\sqrt{35}}{128\sqrt{2}} \eta [\eta \cos 3\beta \sin 4\alpha + \cos \beta (24 \sin^2 \beta \sin 2\alpha \\ &\quad + 7\eta \sin 4\alpha)] \sin^4 \theta \end{aligned}$$

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