Nuclear Electric Quadrupolar Interactions in NMR Spectroscopy- An Introduction

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• Electric Interactions - General
• Nuclear electric quadrupole moments
• Electric field gradients
• The Quadrupolar Hamiltonian – NQR Spectroscopy
• Influence on the NMR Spectra
  – Static Solid NMR Lineshapes
  – MAS-NMR Spectra
  – Nutation Behavior
  – Quantification Aspects
• Applications in Solid State/Materials Chemistry
Nuclear electric quadrupole moment:
non-spherical distribution of nuclear charge

A  B  C  D

$I = 0$  $I = 1/2$  $I \geq 1 ; eQ > 0$  $I \geq 1 ; eQ < 0$

eQ $\sim 10^{-25}$ to $10^{-30}$ m$^2$
This quadrupole moment interacts with local electric field gradients created by the bonding environment of the nuclei. 

-> probe of local symmetry
Nuclear spin values

Anzahl

Spin

0,5 1,0 1,5 2,0 2,5 3,0 3,5 4,0 4,5 5,0 5,5 6,0 6,5 7,0 7,5 8,0

10B 138La 50V 176Lu

32 32 23 18 9
### Solid State NMR Periodic Table

| Element | \(^2\text{H}\) | \(^7\text{Li}\) | \(^9\text{Be}\) | \(^{23}\text{Na}\) | \(^{25}\text{Mg}\) | \(^{39}\text{K}\) | \(^{43}\text{Ca}\) | \(^{45}\text{Sc}\) | \(^{49}\text{Ti}\) | \(^{51}\text{V}\) | \(^{53}\text{Cr}\) | \(^{55}\text{Mn}\) | \(^{57}\text{Fe}\) | \(^{59}\text{Co}\) | \(^{61}\text{Ni}\) | \(^{63}\text{Cu}\) | \(^{65}\text{Zn}\) | \(^{71}\text{Ga}\) | \(^{73}\text{Ge}\) | \(^{75}\text{As}\) | \(^{77}\text{Se}\) | \(^{79}\text{Br}\) | \(^{87}\text{Kr}\) | \(^{89}\text{Y}\) | \(^{91}\text{Zr}\) | \(^{93}\text{Nb}\) | \(^{95}\text{Mo}\) | \(^{99}\text{Tc}\) | \(^{103}\text{Rh}\) | \(^{105}\text{Pd}\) | \(^{109}\text{Ag}\) | \(^{113}\text{Cd}\) | \(^{115}\text{In}\) | \(^{119}\text{Sn}\) | \(^{121}\text{Sb}\) | \(^{125}\text{Te}\) | \(^{127}\text{I}\) | \(^{131}\text{Xe}\) | \(^{133}\text{Cs}\) | \(^{137}\text{Ba}\) | \(^{139}\text{La}\) | \(^{179}\text{Hf}\) | \(^{181}\text{Ta}\) | \(^{183}\text{W}\) | \(^{185}\text{Re}\) | \(^{187}\text{Os}\) | \(^{191}\text{Ir}\) | \(^{193}\text{Pt}\) | \(^{197}\text{Au}\) | \(^{201}\text{Hg}\) | \(^{205}\text{TI}\) | \(^{207}\text{Pb}\) | \(^{209}\text{Bi}\) | \(^{210}\text{Po}\) | \(^{211}\text{At}\) | \(^{217}\text{Rn}\) | \(^{223}\text{Fr}\) | \(^{225}\text{Ra}\) | \(^{227}\text{Ac}\) | \(^{232}\text{Th}\) | \(^{238}\text{U}\) | \(^{244}\text{Pu}\) | \(^{246}\text{Am}\) | \(^{252}\text{Cf}\) |
|---------|-----|------|------|--------|--------|-------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|

- **Red**: Standard
- **Yellow**: Mössbauer isotope available
- **Pink**: NMR restricted by quadrupolar interactions
- **Blue**: Dominant quadrupolar interaction
- **Orange**: Very small magnetic moment

*(Standard)*

*(Mössbauer isotope available)*

*(NMR restricted by quadrupolar interactions)*

*(Dominant quadrupolar interaction)*

*(Very small magnetic moment)*
The electrostatic interaction

\[ E_{el} = \int \rho(\vec{r})V(\vec{r})d\tau \]

\[ V(\vec{r}) = V(0) + \sum_{\alpha} x_{\alpha} \left( \frac{\partial V}{x_{\alpha}} \right)_{r=0} + \frac{1}{2!} \sum_{\alpha,\beta} x_{\alpha} x_{\beta} \left( \frac{\partial^2 V}{x_{\alpha} x_{\beta}} \right)_{r=0} + \ldots \]

\[ E_{el} = V(0) \int \rho d\tau + \sum_{\alpha} V_{\alpha} \int x_{\alpha} \rho d\tau - \frac{1}{2!} \sum_{\alpha,\beta} V_{\alpha,\beta} \int x_{\alpha} x_{\beta} \rho d\tau + \ldots \]

Coulomb term    dipole term    quadrupole term

\[ V_{\alpha} \equiv \left( \frac{\partial V}{\partial x_{\alpha}} \right)_{r=0} \]

Cartesian electric field components

\[ V_{\alpha,\beta} \equiv \left( \frac{\partial^2 V}{\partial x_{\alpha} \partial x_{\beta}} \right)_{r=0} \]

Cartesian electric field gradient components
Electric field gradient

Symmetric second-rank tensor diagonal in the principal axis system

\[ \nabla E_{\alpha,\beta} = \begin{bmatrix} V_{xx} & V_{xy} & V_{xz} \\ V_{yx} & V_{yy} & V_{yz} \\ V_{zx} & V_{zy} & V_{zz} \end{bmatrix} \]

Laplace equation

\[ V'_{xx'} + V'_{yy'} + V'_{zz'} = 0 \]

2 parameters:

\[ V'_{z'z'} = \text{eq} \quad \text{and} \quad \eta = \frac{V'_{y'y'} - V'_{x'x'}}{V'_{z'z'}} \]

Absolute size deviation from cylindrical symmetry
The Quadrupolar Hamiltonian

\[ E_{el} = V(0) \int \rho d\tau + \sum_{\alpha} V_{\alpha} \int x_{\alpha} \rho d\tau - \frac{1}{2!} \sum_{\alpha, \beta} V_{\alpha, \beta} \int x_{\alpha} x_{\beta} \rho d\tau + \ldots \]

- **Coulomb term**
- **dipole term**
- **quadrupole term**

\[ Q_{\alpha\beta} = \int \left( 3x_{\alpha} x_{\beta} - \delta_{\alpha\beta} r^2 \right) \rho d\tau \]

\[ E_{Q} = \frac{1}{6} \sum_{\alpha, \beta} V_{\alpha\beta} Q_{\alpha\beta} \]

\[ \hat{Q}_{\alpha\beta} = \left[ \frac{3(\hat{I}_{\alpha} \hat{I}_{\beta} + \hat{I}_{\beta} \hat{I}_{\alpha})}{2} - \delta_{\alpha\beta} \hat{I}^2 \right] \frac{eQ}{I(2I-1)} \]

\[ \hat{H}_{Q} = \frac{e^2 qQ}{4I(2I-1)} \left[ \left( 3\hat{I}_{z'}^2 - \hat{I}^2 \right) + \eta \left( \hat{I}_{y'}^2 - \hat{I}_{x'}^2 \right) \right] \]

**Expressed in spin coordinates**

**Wigner-Eckart-Theorem**
Orientational quantization of spins along the EFG axis results in energy splittings.

Spin-3/2

$|\pm 3/2>$

$|\pm 1/2>$

Spin-5/2

$|\pm 5/2>$

$|\pm 3/2>$

$|\pm 1/2>$

Spin-7/2

$|\pm 7/2>$

$|\pm 5/2>$

$|\pm 3/2>$

$|\pm 1/2>$

Nuclear quadrupole resonance („Zero-field NMR“)
Effect of the Quadrupolar Interaction on the NMR Spectra

For $H_Q \sim 0.05 H_z$: first-order perturbation theory sufficient.

\[
\hat{H} = \hat{H}_0 + \hat{H}_Q
\]

\[
E_m^{(1)} = E_m^{(0)} + \langle m|H_Q|m\rangle
\]

Case of axial symmetry ($\eta = 0$)

\[
\hat{H} = -\gamma \hbar B_o \hat{I}_z + \frac{e^2 q Q}{4I(2I-1)} \left[ 3\hat{I}_z^2 \cos^2 \theta + 3\hat{I}_x^2 \sin^2 \theta 
+ 3(\hat{I}_z \hat{I}_x + \hat{I}_x \hat{I}_z) \sin \theta \cos \theta - \hat{I}^2 \right]
\]
For axially symmetric EFG, the 1st order correction is:

\[ \langle m|\hat{H}_Q|m \rangle = \frac{e^2 q Q}{4I(2I - 1)} \left[ 3m^2 \cos^2 \theta + \frac{3}{2} I(I + 1) \sin^2 \theta - \frac{3}{2} m^2 \sin^2 \theta - I(I + 1) \right] \]

\[ E_m^{(1)} = -m\gamma \hbar B_o + \frac{e^2 q Q}{4I(2I - 1)} \left[ 3m^2 - I(I + 1) \right] \frac{3\cos^2 \theta - 1}{2} \]

Energy level diagram for \( I = 3/2 \)

\( \Theta = 90^\circ \)

\( \Theta = 0^\circ \)
Powder samples: orientational averaging case $I = 3/2$

Central transition

Satellite transitions
Powder pattern for spin-7/2

Energy

-7/2

-5/2

-3/2

-1/2

1/2

3/2

5/2

7/2

Central transition

Satellite transitions
Stronger Quadrupole Coupling:

Second-order perturbation theory

\[ \hat{H} + \hat{H}_Q^{(1)} \]

\[ \hat{H} + \hat{H}_Q^{(2)} \]

\[ \hat{H}_Z \]

\[ B_0 = 0 \]

\[ m = -3/2 \]

\[ m = -1/2 \]

\[ m = 1/2 \]

\[ m = 3/2 \]

anisotropic
More complicated geometry dependence of the second-order quadrupolar perturbation

\[ E_m^{(2)} = \sum_{m'} \frac{\langle m'H_Q|m'\rangle \langle m'|H_Q|m\rangle}{(E_{m'} - E_m)} \]

inverse dependence on the Larmor frequency

For axial symmetry:

\[ E_m^{(2)} = -\hbar \nu_Q^2/12\nu_o \times m \{ 3/2 \cos^2\theta(1-\cos^2\theta)(8m^2-4l(l+1) + 1) + 3/8(1-\cos^2\theta)^2 (-2m^2 + 2l(l+1) - 1) \} \]

For the central \(|1/2> \leftrightarrow |-1/2>\) coherence:

\[ \nu = -\nu_Q^2/16 \nu_o \times \{l(l+1) - 3/4(1-\cos^2\theta)(9\cos^2\theta-1) \} \]

where \(\nu_Q = 3C_Q/2l(2l-1)\)

second-order quadrupolar shift
Anisotropic lineshape broadening caused by electric quadrupolar interactions

1st order

2nd order

\[ \eta = 0 \]

\[ \eta = 0.5 \]

\[ \eta = 1 \]
Effect of MAS on lineshape

$^{23}\text{Na}$ MAS-NMR of $\text{T} - \text{Na}_3\text{PO}_4$

Linewidth decreases with increasing field strength
Resonance frequency increases with increasing $B_0$
Composite shapes are field dependent
$^{11}\text{B MAS in borate glasses}$

Trigonal planar $D_{3h}$

Three-coord. $C_{2v}$

Tetrahedral $T_d$
$^{23}\text{Na MQMAS @ 30kHz of crystalline Na}_2\text{PO}_3\text{F}$

Parameters calculated from the center of gravity

- **Na(I):** $P_q = 2.3$ MHz, $\delta_{\text{iso}} = 2.3$ ppm
- **Na(II):** $P_q = 2.5$ MHz, $\delta_{\text{iso}} = 0.4$ ppm
- **Na(III):** $P_q = 3.2$ MHz, $\delta_{\text{iso}} = -5.9$ ppm
- **Na(IV):** $P_q = 2.7$ MHz, $\delta_{\text{iso}} = -4.8$ ppm
Spectral simulation of each $^{23}\text{Na}$ site resolved in the F1 dimension

- **Na(I)**
  - $C_q = 1.98 \text{ MHz}$
  - $\delta_{iso} = 3.1 \text{ ppm}$
  - $\eta = 0.64$

- **Na(II)**
  - $C_q = 2.38 \text{ MHz}$
  - $\delta_{iso} = 0.65 \text{ ppm}$
  - $\eta = 0.47$

- **Na(III)**
  - $C_q = 3.0 \text{ MHz}$
  - $\delta_{iso} = -6.1 \text{ ppm}$
  - $\eta = 0.50$

- **Na(IV)**
  - $C_q = 2.37 \text{ MHz}$
  - $\delta_{iso} = -5.1 \text{ ppm}$
  - $\eta = 0.72$

L. Zhang, C. Fehse, J. Vannahme, H. Eckert, to be published
Deconvolution of the MAS-NMR lineshape

Impurity NaF

L. Zhang, C. Fehse, J. Vannahme, H. Eckert, to be published
The intensity distribution of 1st order quadrupolar ssb-s is sensitive to the EFG asymmetry parameter (I = 7/2).
Higher Resolution in the satellite transitions

\[ \nu^{(2)}(m) = \nu_L \sigma_{QS}(m) + \frac{3}{128} \frac{C_Q^2}{\nu_L} \frac{6I(I+1) - 34m(m-1) - 13}{I^2(2I-I)^2} g(\alpha, \beta, \eta) \]

isotropic part

\[ \sigma_{QS}(m) = \frac{3}{40} \frac{C_Q^2}{\nu_L^2} \frac{I(I+1) - 9m(m-1) - 3}{I^2(2I-1)^2} \left(1 + \frac{1}{3} \eta^2\right) \]

anisotropic part

2nd order effects greatly diminished for \(|\pm 1/2> \leftrightarrow |\pm 3/2>\) coherences (I = 5/2)
and for \(|\pm 3/2> \leftrightarrow |\pm 5/2>\) coherences (I = 9/2)

27Al NMR of aluminoborate glass (7.0 T)

Excitation Behavior of Q-nuclei

The effective nutation frequency depends on the ratio $\nu_Q/\nu_1$.

There are two distinct regimes:

**Non-selective excitation limit:** $\nu_Q << \nu_1$:
- Effective rf amplitude is identical to $\nu_{liq}$ measured in liquids.
- All the Zeeman transitions are being observed.

**Selective excitation limit:** $\nu_Q >> \nu_1$:
- Effective rf nutation frequency is given by $(I + \frac{1}{2}) \nu_{liq}$.
- Only the central $|1/2\rangle \leftrightarrow |-1/2\rangle$ coherence is detected.

![Diagram](image)
2-D Nutation NMR Spectroscopy

FIG. 3. Calculated nutation spectra for an isolated spin $I = \frac{3}{2}$ as function of the ratio $\omega_0/\omega_{rf}$, with $\eta = 0$. No resonance offset is taken into account. The scale factors of the spectra are 1, 4.7, 15.2, 14.9, 10.2, 7.3, 5.7, and 3.0 with respect to the $\omega_0/\omega_{rf} = 0$ spectrum. In all spectra a Lorentzian line broadening of 2.5 kHz was applied.

Kentgens et al., J. Magn. Reson. 71 (1987), 62
Spin Echo measurements of homodipole couplings between Q-nuclei
23Na Spin Echo Decay Spectroscopy

\[
\frac{I(2t_1)}{I_0} = \exp \left[ -\frac{M_{2d}^{II}}{2} (2t_1)^2 \right]
\]

\[
M_{2d}^{II} = F(I) \left( \frac{\mu_0}{4\pi} \right)^2 \gamma^4 \hbar^2 \sum_j \left\{ \frac{3}{2} \left( \frac{1-3\cos^2 \theta}{r_{ij}^3} \right)^2 \right\}
\]

Regime of validity:
\[ H_Q^{(2)} \sim H_D \ll H_1 \ll H_Q^{(1)} \]
(selective excitation)
low temperatures (~100 K)
(no dynamic contribution)
Example of Spin Echo Curve

\[
\frac{I(2\tau)}{I(0)} = \exp\left[-\frac{(2\tau)^2 M_{2d}}{2}\right]
\]

for: \(2\tau \leq 0,2\text{ms}\)
$^2{\text{Na}}$ Spin Echo Decay: Model Compounds

$B_0 = 7.04T$

$B_0 = 9.40T$

$M_2 = 0.9562 \left(\frac{\mu_o}{4\pi}\right) \gamma^4 h^2 \sum r_{ij}^{-6}$

Spatial sodium distribution in oxide glasses

$M_2$ ($^{23}$Na -$^{23}$Na) vs. number density

- Sodium silicate glasses
- Sodium borate glasses
Spectra of spin-1/2 nuclei coupled to quadrupolar nuclei

$^{31}$P MAS-NMR of (CuI)$_3$P$_4$S$_4$

Practical Aspects

Dipolar multiplets become asymmetric in case of strong Q-interactions.

Indirect determination of $C_Q$ even if direct observation fails owing to too strong interaction.

Indirect determination of $C_Q$ also possible via S[I] TRAPDOR experiments, stepping the irradiation frequency of the recouple nucleus $I$.

Sometimes spin-1/2 nuclei are broad/unobservable, when strongly coupled with quadrupolar nuclei: certain C-N, C-Cl, C-Br groups in $^{13}$C CPMAS.
Further important topics

• Resolution Enhancement via MQ-excitation:

• Spin-locking and CPMAS of quadrupolar nuclei:

• Re-coupling dipolar interactions with quadrupolar nuclei

• Signal Enhancement via Population Transfer

• Dynamic Information via Modulation of Quadrupolar Interactions
Literature

• A. Abragam (1961), Principles of nuclear magnetism, Oxford University Press.
• D. Freude, J. Haase, NMR-Basic Principles and Progress 29 (1993), 3
Fig. 1. Energy levels, populations (in parentheses), and NMR spectra of a quadrupolar spin-5/2. (a) In thermal equilibrium. (b) After selectively inverting the satellite transitions in the order 2, 1, −2, −1. The intensities in the NMR spectrum of (b) are changed by the factors indicated near each line. In particular, the central transition intensity is enhanced by a factor of five.
Comparison of experimental and calculated (WIEN2k) $^{45}$Sc quadrupole $C_Q$-values in intermetallic compounds

C. Fehse, T. Harmening, R. Pöttgen, H. Eckert, to be published
Fig. 2. Frequency-sweep method to adiabatically invert the satellite transitions in the sequence 2, 1, −2, −1. This will yield the populations of fig. 1b. The time dependence of the applied frequency \( \omega \) is shown together with the timing of the rf envelope for both frequency sweeps and the inspection pulse.
Results on $\text{Al}_2\text{O}_3$

**FIG. 5.** Oxygen-17 CP spectra of $\sim 10\%$ $^{17}$O-enriched corundum powder, at 8.3 T. (a) Sweep enhancement of the $^{27}$Al prior to CP; 64 acquisitions. (b) Without sweep enhancement of $^{27}$Al; 128 acquisitions. The display gains have been normalized for the different numbers of acquisitions. The repetition time was 200 s in both cases.