Search for nuclear quadrupole resonance in an organic quantum magnet

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Theory of the nuclear quadrupole resonance spectroscopy
Consider a single nucleus in its electronic environment ... this is the electrostatic energy of a charge in fields written in terms of multipole moments.

The traceless quadrupole moment tensor is the familiar expression.
Electric field gradient (EFG) $V^{ij}$

$$U_q = \frac{1}{6} Q_{ij} V^{ij}$$

$V_{xx} + V_{yy} + V_{zz} = 0$

$|V_{xx}| \leq |V_{yy}| \leq |V_{zz}|$

$$eQ = \int (3z^2 - r^2) \rho(x) d^3x$$

Quadrupole interaction energy with field.

Laplace’s equation -> EFG is traceless.

Choice of axes permit ordering eigenvalues of EFG by convention

Cylindrical symmetry -> only one non-vanishing quadrupole moment
Only *two* independent parameters

\[ \eta = \frac{V_{yy} - V_{xx}}{V_{zz}} \]

Assymetry parameter

\[ V_{xx} = V_{yy} = -\frac{eq}{2} \]

\[ V_{zz} = eq \]

\[ Cq = e^2qQ \text{ is the “quadrupole coupling constant.”} \ q \text{ is a measure of our ignorance.} \]
NQR transition frequencies

\[ H_q = A \{3I_z^2 - I^2 - \frac{\eta}{2}(I_+^2 + I_-^2)\} \]

\[ A = \frac{e^2 q Q}{4I(2I - 1)} \]

\[ \langle m | H_q | m' \rangle = \frac{e^2 q Q}{4I(2I - 1)} \left[3m^2 - I(I + 1)\right] \delta_{mm'} \]

Hamiltonian for quadrupole interaction of nucleus with external field

...matrix elements...

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

energy levels
NQR transition frequencies

\[ \hbar \omega_m = E_{m+1} - E_m \]

\[ \omega_m = \frac{3A}{\hbar} (2|m| + 1) \]

\[ A = \frac{e^2 qQ}{4I(2I - 1)} \]

See more:
http://www.phys.ufl.edu/~majewski/nqr/equation.pdf
Spin 1 transition frequencies (14N)

- For non-axial field gradients, nitrogen has two principle transition frequencies and a third low frequency transition being the difference

\[
\omega_{\pm} = \frac{3}{4} \frac{e^2 qQ}{\hbar} \left( 1 \pm \frac{\eta}{3} \right)
\]
\[
\Delta \omega = \frac{e^2 qQ}{\hbar} \frac{\eta}{2}
\]
Spin 3/2 transition frequencies (35Cl)

- For non-axial field gradients, chlorine has on transition frequency

\[
\omega_Q = \frac{6A}{\hbar} \sqrt{1 + \frac{\eta^2}{3}} = \frac{e^2 q Q}{2\hbar} \sqrt{1 + \frac{\eta^2}{3}} = \frac{1}{2} C_Q \sqrt{1 + \frac{\eta^2}{3}}
\]
Nuclear Quadrupole Resonance (NQR) - applications
NATO – interest in NQR

• NATO Science for Peace and Security Series publishes annual “Magnetic Resonance Detection of Explosives and Illicit Materials” bulletin
• NQR employs non-invasive radio frequency methods
• Can penetrate luggage
• Is chemically specific
• Challenge: low sensitivity – signal to noise ratio limits practical application
• 2014 edition: 14 studies, 168 pages ...
  excerpt
14N NQR is a chemical fingerprint for explosives and narcotics

• The NQR signal unambiguously identifies a molecular structure

• Land Mine Detection - As of 29 July 2014, there were 587.2 square kilometers (226.7 square miles) of Croatian territory suspected to contain land mines. These areas are located in 11 counties and 82 cities and municipalities.

• TSA – airport bag scanner

• DEA – MDMA, methamphetamine, heroine all have known NQR spectra (mail scanning?)

Fig. 1.5 NQR baggage scanner T-3-03

• Implement automatic calibration and self-test capabilities.
• Increase the number of digital acquisition channels.
• Reduce the overall cost of manufacture.
NQR for interesting solid state physics (non-terrorist related)

• NQR is extremely sensitive to electronic environment and atomic positions and local fields of a given nucleus

• NQR can determine chemically inequivalent sites

FIG. 1. Schematic representation of perovskite-type layer in \((C_nH_{2n+1}NH_3)_2MnCl_4\).
NQR for interesting solid state physics (non-terrorist related)

- NQR can characterize
  - Structural phase transitions (by the $T$-dependence of NQR frequencies)
  - Molecular motions in solids
  - Bonding characteristics, crystal geometry
  - Condensed matter: order/disorder properties, ferroelectric properties, affects of doping -> magnonetic transitions of quasiparticles (AFM ordering, BEC, bose glass)

FIG. 2. Temperature dependence of the two $^{35}\text{Cl}$ NQR frequencies in $(\text{CH}_3\text{NH}_2)_2\text{MnCl}_4$. 
My science objectives

1. Develop contemporary NQR techniques

2. Investigate interesting materials with NQR with new methodology
1. Develop NQR as a technique

- Increase the SNR for NQR, especially for low frequency as applied to explosives
- Develop methods to determine unknown NQR frequencies (this is hard)
- Focus on the problematic SNR at low frequencies
- Investigate NQR/NQR cross polarization in perovskite-types for explosives detection (uncharted territory)
2. Investigate interesting materials with NQR

• Complete NQR studies on interesting systems revealing new physics
• Complete electronic structure calculations
• Further existing but incomplete NQR studies using techniques developed (there are many)
• All the while focusing on low frequency NQR collection, furthering agenda of landmine detection (thus, an emphasis on organic metal complexes)
• Investigate level crossing for 14N detection with poor SRN (uncharted territory)
“Most explosives contain quadrupolar nuclei (nitrogen-14) the spectral lines of which are usually located at low RF frequencies. The signal intensity in this frequency range is quite low because the low energy difference between excitation levels. Another issue is external and internal interference and spurious signals. All these problems are solved by using optimized NQR detection technique, equipment and signal processing.” NATO Science for Peace and Security Series B – “Magnetic Resonance detection of explosives and illicit Materials” (2014)
Superheterodyne Spectrometer

- Perfectly phase locked: 20 MHz computer clock coherent with transmit and receive functions
- Easy change, high quality band sensitive components
- Pulse sequences completely programmable
- 2 channel X, Y
- Signal averaging with real time FFT
Pulse Generator — overview

http://www.phys.ufl.edu/~majewski/nqr/superhettimelines.zip
Pulse generator - details

http://www.phys.ufl.edu/~majewski/nqr/superhetdetails.zip
Transmitter optimizations

- Band selectivity
- Crossed diodes (hundreds of them in series)
  - This actually had remarkable affect on S/N.
Receiver section

- 20 MHz
  - From PD of pulse generator section

- f + 20 MHz (from NMR generator chain)

- NMR signal from fast recovery amplifier (50 dB)

- ZX05-1+

- Mixer (-6dB)

- JSPHS-26
  - Phase shift (controlled by DC voltage from 10 t pot on front panel)

- 20 MHz reference

- SBP-21.4+

- ZFL-1000LN

- F
  - Narrow band 20 MHz IF chain
  - F = narrow band filter

- A
  - A = low noise (20 dB each) broadband amplifier

- I & Q Demodulator

- MIQA-21D+

- Outputs
  - Filters
  - X
  - Q
  - Y
Generator and receiver – side by side

- Generator:
  - 20 MHz Oscillator (20MHz)
  - Logic Pulses (A Q phase, B 90 phase)
  - IQM use as 2-channel gate

- Receiver:
  - IQM=I&Q Network Narrow Band at 20 MHz
  - Narrow band 20 MHz IF chain
  - F = narrow band filter
  - A: low noise (20 dB each broadband amplifier)

- Other Components:
  - PD: Power Detector
  - Diodes: Coded/Decoded Diodes
  - SMA Connectors
  - Filters
  - Mixers
  - Demodulators
  - Outputs (X, Y, F, Q)
Probe section

NMR Probe Electronics

Simple Single Frequency Tank Circuit

[Image of a circuit diagram showing components such as capacitors (CM, CT), inductors (L), and other electronic parts]

http://www.phys.ufl.edu/~majewski/superhetdetails.zip
http://www.phys.ufl.edu/~majewski/nqr/nqr-combined.pdf
http://www.github.com/Altoidnerd/nmr-tank-circuits
isolation – hybrid tee

BRIDGE OF RF EXCITATION AND SIGNAL RECEPTION

- RF Excitation Pulses
- Hybrid Tee (different tees for different frequency bands)
- Fast recovery broadband amplifier
- 50 Ohm terminator
- Tuning & Matching Box
- Cryogenic cable (n* half wavelengths)
- Tuning at
- NMR coil
- NMR Coil
Receiver, probe, bridge optimizations at 30 MHz (NaClO3 control)

- High quality RF amplifiers
- Homemade IF state – TL082 + LM386
- Band pass filters
- Fixed ground plane, star topology, short leads
- Rigid coil eliminates mechanical oscillations
- Heavy shielding
- Brass vs aluminum
- Shortened interconnects
- Quarter wave transmission line transformer replaces magic tee
Isolation optimization – quarter waves (double S/N)
2 control samples covering 3-30 MHz

- NaClO3 (sodium chlorate) with expected 35Cl NQR @ 29 MHz
- HMT (hexamethylenetetramine) with expected NQR @ 3 MHz
NaClO3 @ 29.92 MHz
vast SNR improvement

NaClO3 response to a transient at 29.963 MHz, pulse width=50us, signal averaging N=500;

Fourier transform (left) of discrete FID (above). res =7204 pixels;
horizontal_axis=100us/div
HMT @ 3.088 MHz – unable to use quarter waves

• Lower frequency presents new challenges:
  • @ 30 MHz for $Q = 50 = L\omega/r = f/\Delta f$; $\Delta f = 600$ KHz. GREAT
  • @ 3 MHz, $Q = 50 \rightarrow 6$ KHz probe bandwidth. BAD
  • For a fixed $L$, capacitances required for matching condition become too large for actual components – see http://www.phys.ufl.edu/~majeski/nqr/nqr-combined.pdf
Nevertheless, SNR is excellent

Note the frequency difference between coherent FID's is approximately \(3298.9 - 3318.0 = 19.1\) KHz. The accepted value of the quadrupole coupling constant for pure HMT is 4543 KHz [J. Mag. Res., 51,26-36 (1983)]. Thus

\[
\nu_q^+ - \nu_q^- = \Delta \nu = \frac{1}{2} C_q \eta
\]

\[
2\Delta \nu = \frac{C_q}{C_q} = \eta
\]

Using \(C_q=4543\) KHz we then estimate an order of magnitude for \(\eta\)

\[
\eta = \frac{(2)(19\text{KHz})}{(4543\text{KHz})} \approx .008
\]

An asymmetry parameter this small may have been undetectable using continuous wave methods, but could easily be resolved using the superhet.
HMT probe and coil – hybrid tee used (1/4 wave infeasible)
Searching for *unknown* NQR

- Can only work in increments of probe bandwidth
- At 30 MHz with Q=50, this is 600 KHz. Not bad
- At 3 MHz for Q=50, only 6 KHz of bandwidth before retune
- Capacitances become very large
- Tuning / rebuilding the probe becomes a serious time sink
Work on tuning and matching

- Approximate impedance matching for NMR is well known
- NQR does not operate at fixed frequency when searching
- Standard tuning methodology does not apply

- The search for unknown NQR requires a systematic method to rapidly develop tuned/matched probes with realistic capacitances on hand, reasonable coil dimensions, and the ability to predict the useful bandwidth of a given probe configuration i.e. calculate the reflection coefficient for a bad mismatch
Work on tuning and matching

- **NATO concurs, having simultaneously recognized the same problem**

- **I wrote a python library** for computing probe characteristics – for the engineering problem = “this is what I have on hand.”
### Work on tuning and matching – capMatch.py

<table>
<thead>
<tr>
<th>Approximate $C_1$</th>
<th>Exact $C_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sqrt{r/Z_0}/\omega^2 L$</td>
<td>$\sqrt{r/Z_0}/\omega^2 L \frac{1}{\sqrt{1-r(Z_0-r)/(L^2 \omega^2)}}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Approximate $C_2$</th>
<th>Exact $C_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1 - \sqrt{r/Z_0}/\omega^2 L$</td>
<td>$1 - \sqrt{r/Z_0-r^2/(\omega^2 L^2)} + r^3/(\omega^2 Z_0 L^2) / \omega^2 L + r^2/L$</td>
</tr>
</tbody>
</table>
Cap and coil selection made easy
Time to search for unknown NQR

- NiCl2 [SC(NH2)2]4 dichloro-tetrakis-thiourea-nickel has good science objective to investigate magnonetic BEC and glass phase
Where to begin?

- Typical Cl NQR: 15-42 MHz
- Typical line width: 10-20 KHz
- 2700 probe tunings?

Conclusion:

Must reduce search space

1. infer from similar compound
2. do DFT quantum chemistry calculation to estimate EFG

Must make tuning and matching systematic
1. Infer from similar compounds

- DTN contains thiourea SC(NH2)2 four times in the unit cell
- The pure 14N NQR spectrum of thiourea crystals is known
- Perhaps the 14N resonances in DTN are not so different
1.1 infer from similar compounds

- MnCl$_4$ [CH$_3$NH$_3$]$_2$ (MAMC) is somewhat structurally similar to DTN
- Like other perovskite-type metal organic complexes, XCl$_4$-[CnH$_{2n+1}$]$_2$; X = Mn, Fe, Cu ...
  has chlorine nqr frequencies that are much lower than what is typical (15-60 MHz)

**FIG. 2.** Temperature dependence of the two $^{35}$Cl NQR frequencies in (CH$_3$NH$_3$)$_2$MnCl$_4$. 
2. Do a quantum chemistry calculation

• I began in 2013 investigating the possibility of calculating the EFG in DTN
• This was carried out in March 2013 at Oxford by Tim Green using CASTEP (closed source) due to a reddit comment
• This was repeated at ETH Zurich in October 2013 with Quantum Espresso (open source)
• I finally confirmed the calculation myself on hydra12 on 8-31-2015 in agreement with Oxford, ETH. 16 cores
GIPAW using Quantum Espresso

• This took me two years to learn to do
• It is difficult, but could be repeated for other compounds of interest (MAMC, MAFC) in less time
• It is an exercise in scripting, manipulation of structure files, and parallel resource management.
• If the calculation does not fail, it is self consistent
### Results of GIPAW calculations for DTN

#### CHLORINE: 2 sites

<table>
<thead>
<tr>
<th>Cq (MHz)</th>
<th>( \eta )</th>
<th>( f_q ) (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.4971</td>
<td>0</td>
<td>4.75</td>
</tr>
<tr>
<td>-0.9388</td>
<td>0</td>
<td>464</td>
</tr>
</tbody>
</table>

#### NITROGEN: 2 sites

<table>
<thead>
<tr>
<th>Cq (MHz)</th>
<th>( \eta )</th>
<th>( f_q ) (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5069</td>
<td>0.3683</td>
<td>2.95, 2.30, 0.645</td>
</tr>
<tr>
<td>3.1866</td>
<td>0.3835</td>
<td>2.69, 2.31, 0.611</td>
</tr>
</tbody>
</table>
Known 14N NQR in Thiourea

NITROGEN: 2 sites

\[ C_q = 3.0996 \text{ MHz} \quad | \quad \eta = 0.3903 \quad | \quad f_q = 2.63, 2.02, 0.609 \text{ MHz} \]

\[ C_q = 3.1216 \text{ MHz} \quad | \quad \eta = 0.3954 \quad | \quad f_q = 2.64, 2.03, 0.617 \text{ MHz} \]

Known 35Cl NQR in MAMC

NITROGEN: NO DATA!

CHLORINE:

\[ C_q = ? \quad | \quad \eta = 0 \quad | \quad f_q = 4.564 \text{ MHz} \]

\[ C_q = ? \quad | \quad \eta \neq 0.7 \quad | \quad f_q = 7.711 \text{ MHz} \]
Outlook - looking for perovskite-type metal complexes to study

- Want to obtain MAMC as a test of superhet at 4+ MHz
- Furthermore investigate perovskite-type materials with NQR studies
- Some have known frequencies, but lack full angular Zeeman data
- Some frequencies unknown

<table>
<thead>
<tr>
<th>Compound</th>
<th>known fq (MHz)</th>
<th>notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnCl4(CH3NH3)2</td>
<td>fq=7.711, 4.564</td>
<td>eta, Cq unknown</td>
</tr>
<tr>
<td>CsPbCl3</td>
<td>fq=7.7</td>
<td>eta, Cq unknown</td>
</tr>
<tr>
<td>RbCdCl3</td>
<td>fq=11.2</td>
<td>poor S/N</td>
</tr>
<tr>
<td>CuCl4(CH3CH2NH3)2</td>
<td>fq=11.1, 11.5</td>
<td>(inequiv)</td>
</tr>
</tbody>
</table>

- most or all of the above have no or incomplete structural phase diagrams
- most or all of the above have similar variants
- these low frequency 35Cl transitions are all accompanied by un-documented 14N transitions – of great interest to explosives detection
- Cross relaxations with 35Cl/14N in metal complex/TNT or RDX?