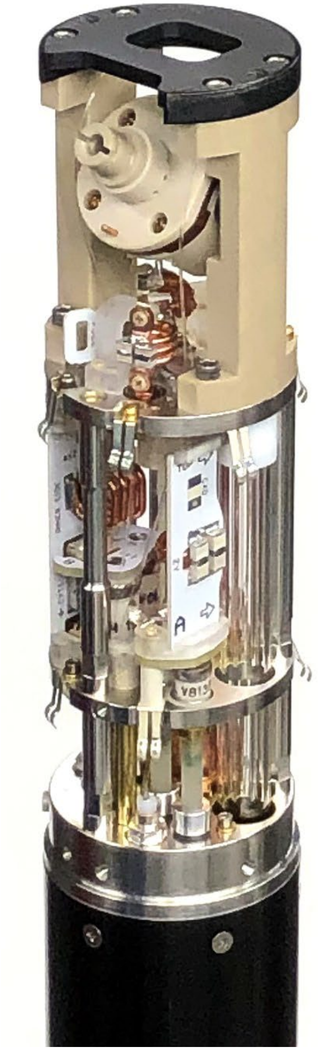
NATIONAL HIGH MAGNETIC FIELD LABORATORY

Building Solid State NMR Probes



Peter Gor’kov

NHMFL

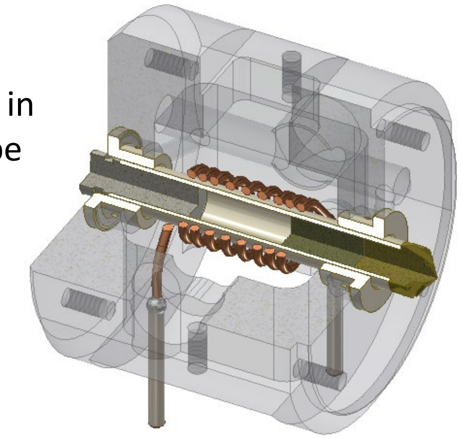
Workshop sponsored by
National Resource for Advanced NMR Technology NIH P41 GM122698

FLORIDA STATE UNIVERSITY

UF UNIVERSITY of FLORIDA

What it is about

MAS spinner in
SS NMR probe



Best ways to attach probe sample coil to NMR spectrometer…

- Basic sample coil matching network
- Examples of multi-resonance matching networks
- Electrical balancing of sample coil and why we do it
- Optimization of channel isolation traps
- ^{1}H-detection probes
- Cross-coils
- Probes for direct detection

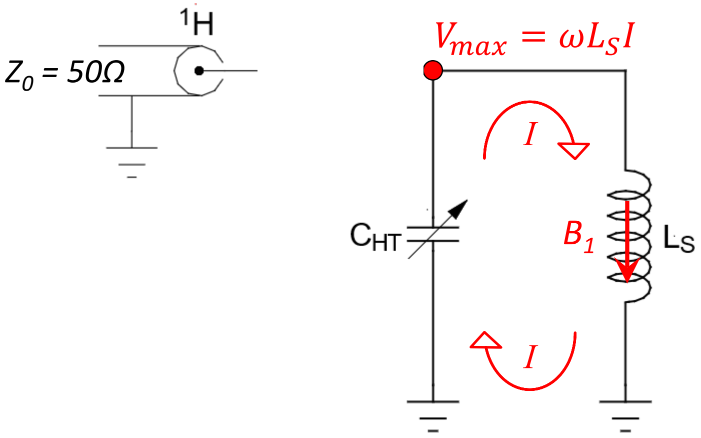
Basic matching network

2022 NRANT Probe Workshop
NIH GM122698

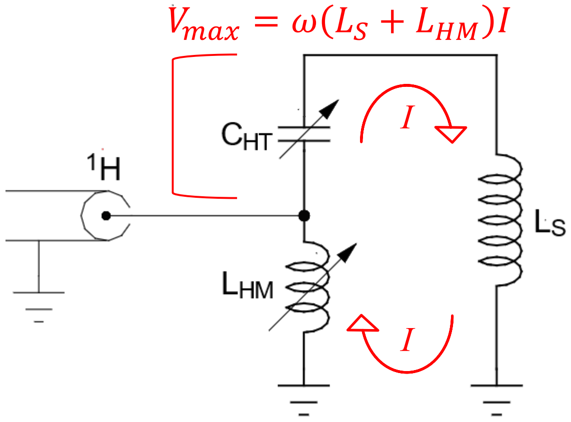
Start from highest frequency ^{1}H channel

Parallel tank circuit L_S-C_{HT} generate large current I in the coil and B_1 field inside sample

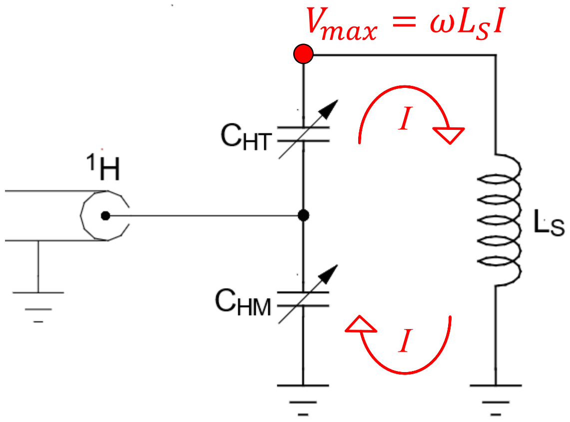
Additional component “matches” circuit impedance to that of 50 Ω spectrometer cable



$$\omega^2 = \frac{1}{L_S(C_{HT} + C_{HM})}$$



$$\omega^2 = \frac{1}{(L_S + L_{HM})C_{HT}}$$



$$\omega^2 = \frac{C_{HT} + C_{HM}}{L_S C_{HT} C_{HM}}$$

Most common

2 high-voltage trimmers

Variable inductor match

1 higher-voltage trimmer

$C_{HM} >> C_{HT} \rightarrow V(C_{HM})$ is low

1 high-voltage trimmer

Smaller footprint

Tunes slightly higher

2-resonance matching network

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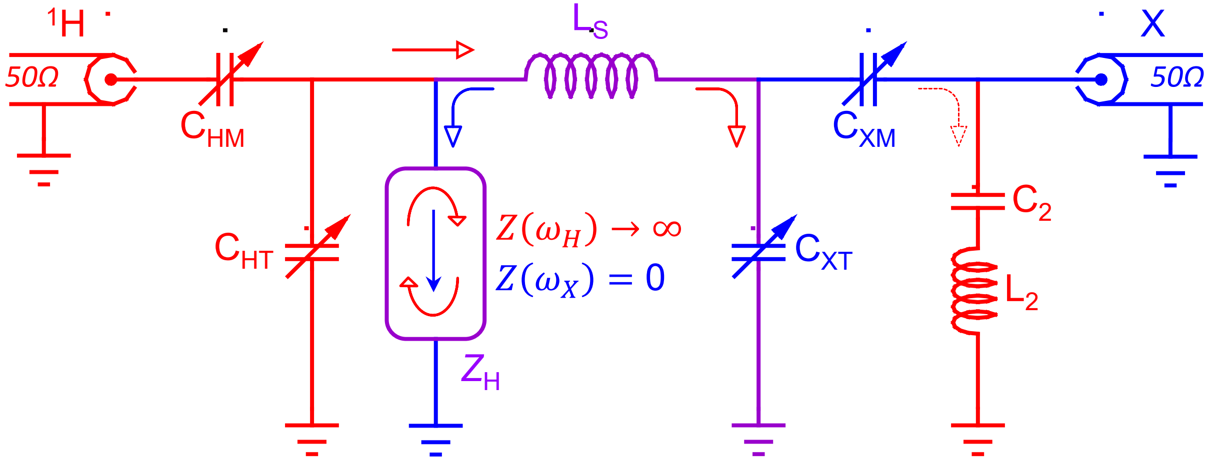
Cross-Hester-Waugh matching network – very common

High and low-frequency inputs are on opposite ends of the coil

Relies on $\omega_X^2 < \omega_H^2$ so that $C_{XT} >> C_{HT}$ becomes path to ground for ^{1}H signal

Resonant trap Z_H adds path to ground for low X frequency while reflecting ^{1}H signal



$$Z(L) = j\omega L$$

$$Z(C) = -\frac{j}{\omega C}$$

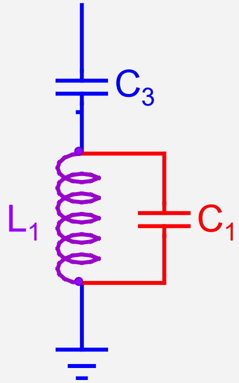
^{1}H/X probe RF circuit. Colors show ^{1}H and X signal paths or their mix.

Examples of Z_H are parallel *L-C* trap or $\lambda_H/4$ coaxial resonator shorted at one end

Any ^{1}H signal still leaking into X port is removed by low-voltage *series* trap L_2-C_2

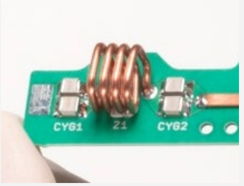
Examples of Z_H isolation traps:

L-C

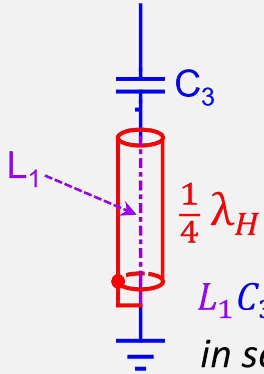


$L_1 C_1 = \omega_H^2$ *in parallel*

$L_1 C_3 = \omega_X^2$ *in series*



Coaxial



$L_1 C_3 = \omega_X^2$

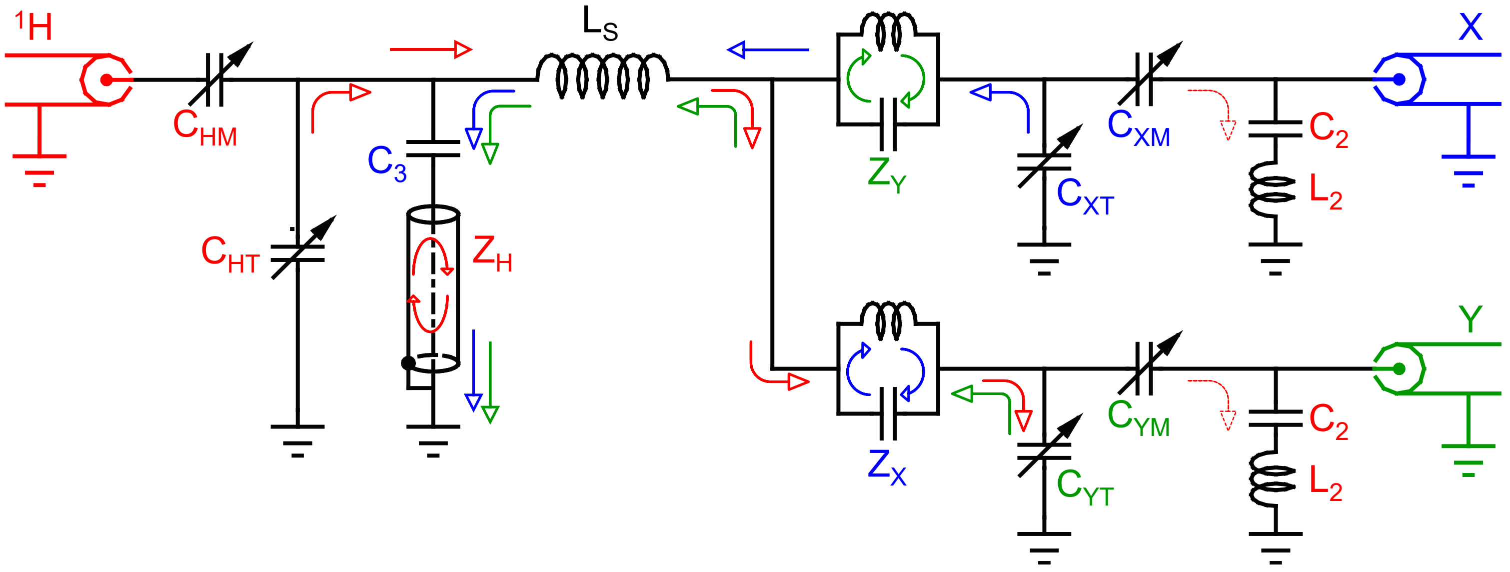
in series

Adding 3rd channel

Addition of 3rd channel Y is done in the similar manner

Reflection trap Z_X is added to isolate X signal from Y-channel circuit

Optional trap Z_Y prevents adjustment of Y channel by X trimmers



Generic 3-resonance 1H/X/Y probe RF circuit, *unbalanced*

4th resonance can be added accordingly

Isolation traps introduce additional RF losses in the circuit

Each additional channel = more isolation traps = probe sensitivity inevitably takes a hit

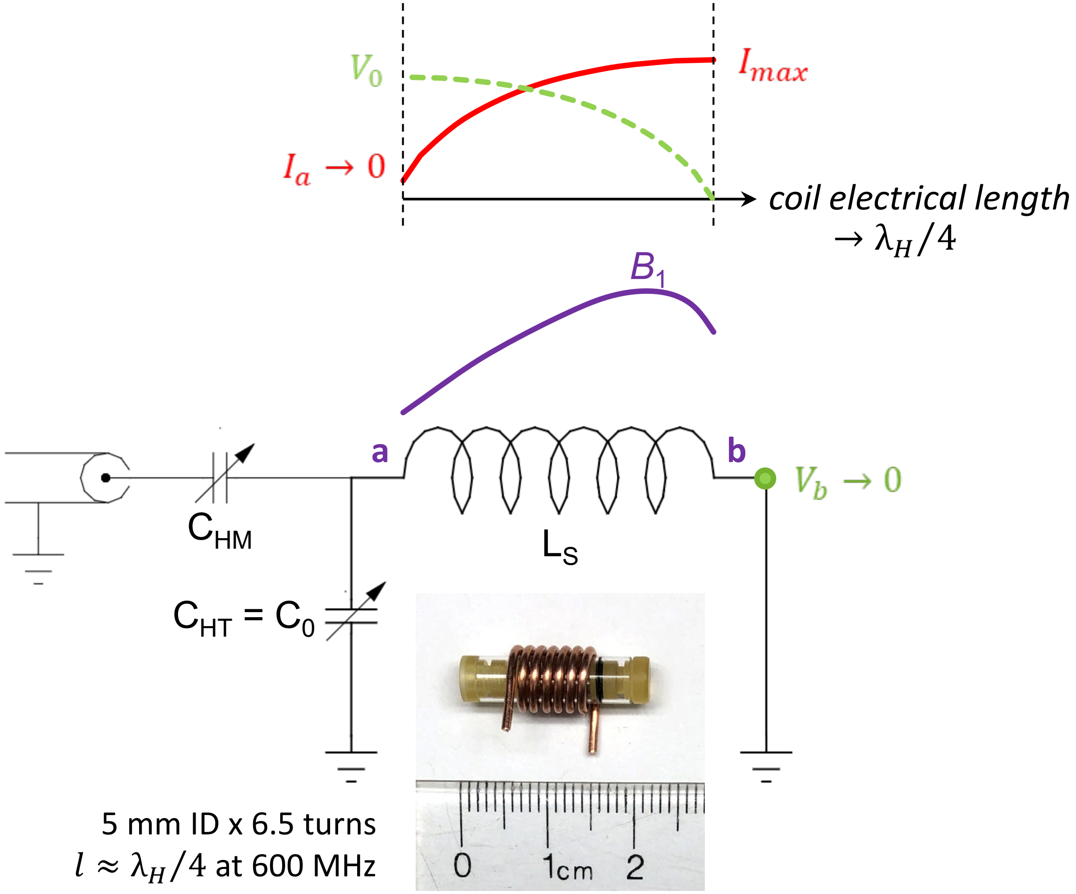
Balancing sample coil – high fields large samples

When coil length approaches $\lambda_H/4$

Coil becomes transmission line with standing waves of V, I

B_1 becomes non-uniform, skewed to grounded coil end

$l \approx \lambda_H/4$ is tuning limit of such circuit



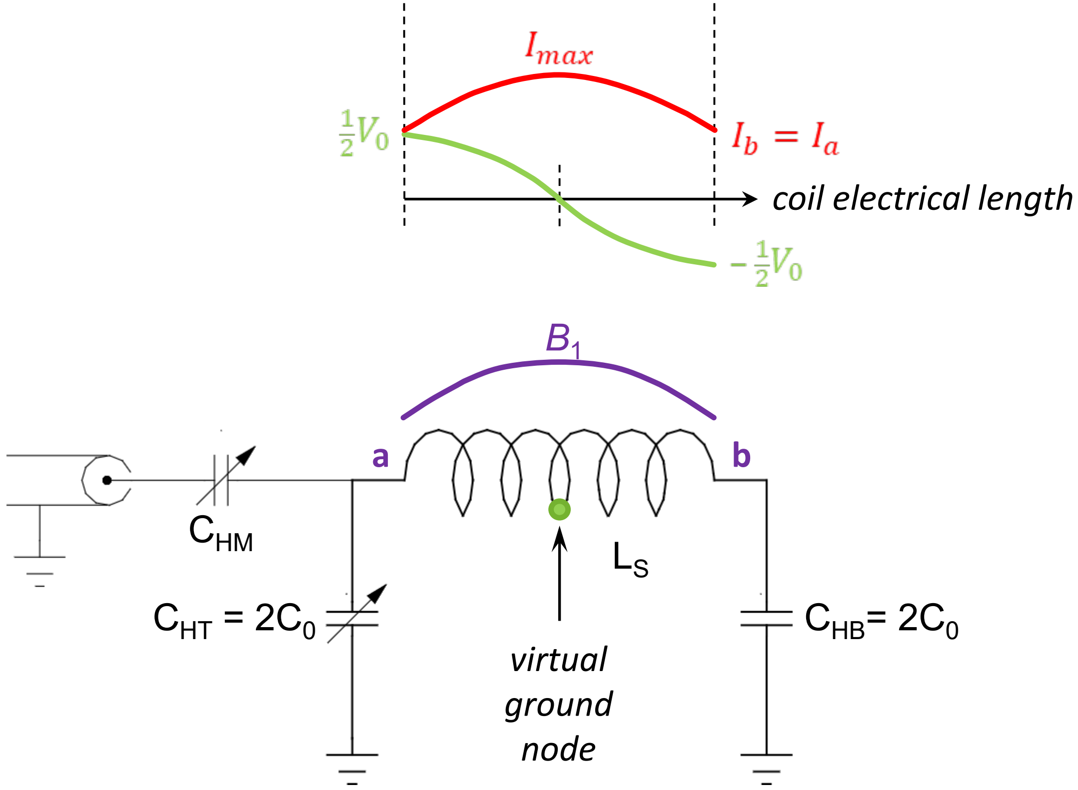
5 mm ID x 6.5 turns
$l \approx \lambda_H/4$ at 600 MHz

COIL BALANCING ungrounds coil with balance capacitor C_{HB}

Circuit tuning limit increases to $l \approx \lambda_H/2$

Standing waves and B_1 field profile regains symmetry

Maximum voltage across circuit is 2X smaller

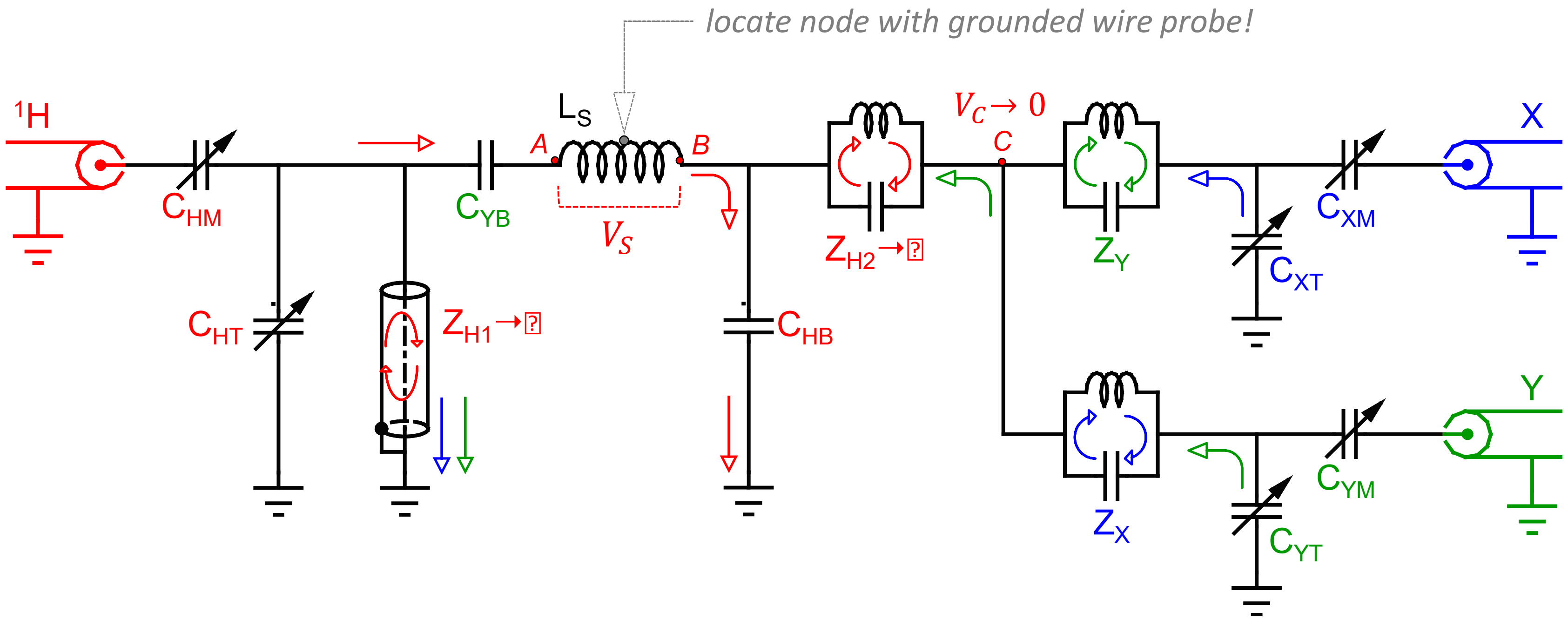


Balancing sample coil

Add second [1]H trap Z_{H2} to redirect [1]H signal to ground via balancing chip C_{HB}

Current symmetry condition $V_A = -V_B = \frac{1}{2} V_S(\omega_H)$ is when coil ends see equal impedance to ground: $C_{HB} \approx C_{HT} + C_{HM}$

Voltage node forms on the coil – locate to verify



Balancing coil at [1]H frequency improves B_1 field homogeneity

[1]H voltages amplitudes are 2X smaller – less arcing risk

Balancing coil at lowest Y frequency is done by adjusting C_{YB} chip – less arcing risk

Balancing at middle frequency X is not simple

3-resonance [1]H/X/Y RF circuit
balanced at [1]H and Y frequencies

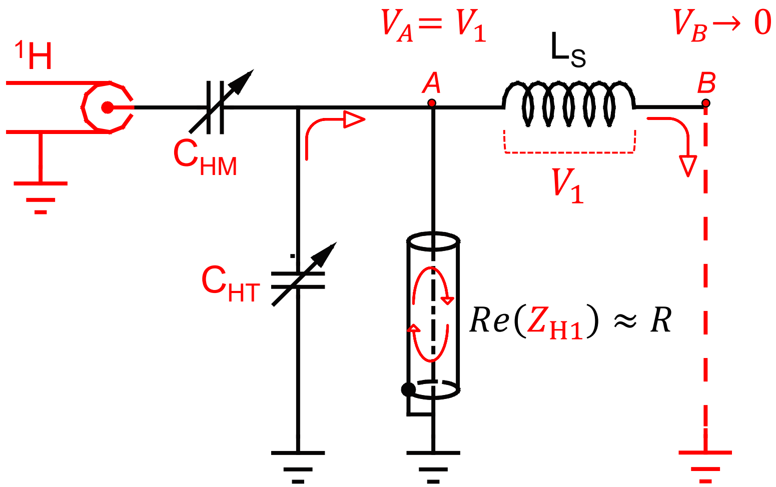
Balancing sample coil – effect on trap loss

Each isolation trap has inherent loss due to internal resonant currents

Will adding 2nd balancing trap Z_{H2} make ^{1}H circuit less efficient?

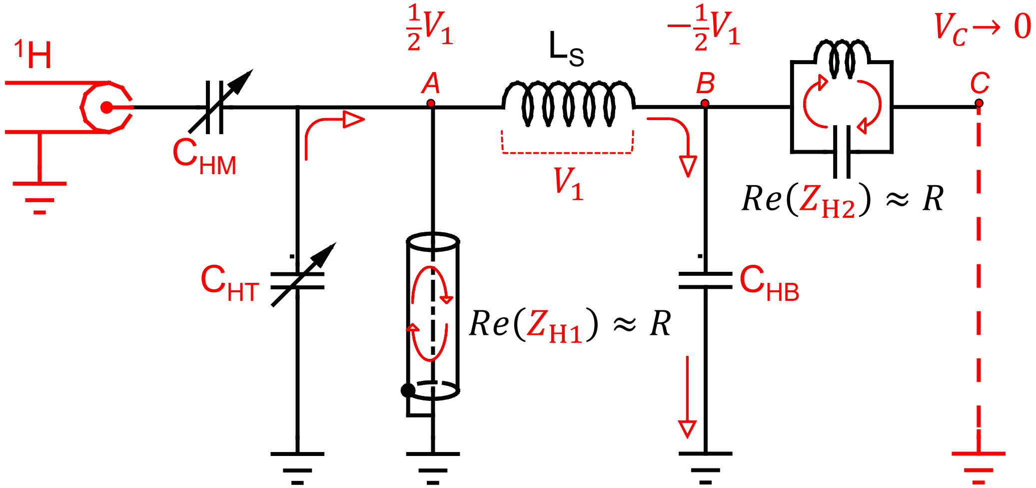
Assume traps Z_{H1} and Z_{H2} have similar losses at ^{1}H frequency: $Re(Z_{H1}) \approx Re(Z_{H2}) = R$

^{1}H-signal loop in ***unbalanced*** circuit



Trap loss: $P_{unb} = \dfrac{V_1^2}{Re(Z_{H1})} = \dfrac{V_1^2}{R}$

^{1}H-signal loop in ***balanced*** circuit



Traps losses: $P_{bal} = \dfrac{\left(\frac{1}{2}V_1\right)^2}{Re(Z_{H1})} + \dfrac{\left(\frac{1}{2}V_1\right)^2}{Re(Z_{H2})} \approx \dfrac{1}{2} \cdot \dfrac{V_1^2}{R} = \dfrac{1}{2} P_{unb}$

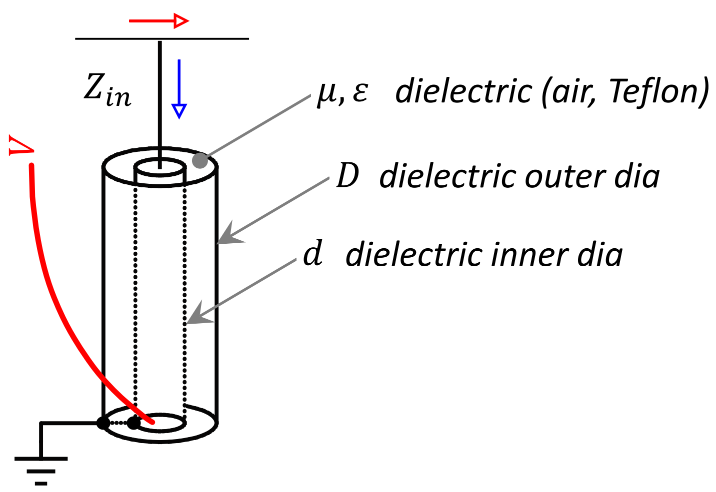
Balancing ^{1}H channel with 2nd lossy element actually improves its sensitivity

NMR probes made for ^{1}H-detection better have balanced sample coil!

Balancing sample coil

- Talk about balancing means little unless voltage balance conditions are checked with grounded wire probe!
- Spare cover with holes in strategic places can help with location of ground nodes on the coil and with ball shift measurements
- Touching sample coil at the location of virtual ground node with a grounded wire probe produces no shift in resonance
- Ideally your ground node will be on the middle turn of the sample coil

Coaxial trap optimization



How to minimize signal loss in coaxial traps? $P_{trap\ loss} = \frac{V}{Re(Z_{in})^2}$

Characteristic impedance of coaxial line $Z_0 \approx \frac{138}{\varepsilon_r} log_{10}\, g \qquad g = \frac{D}{d}$

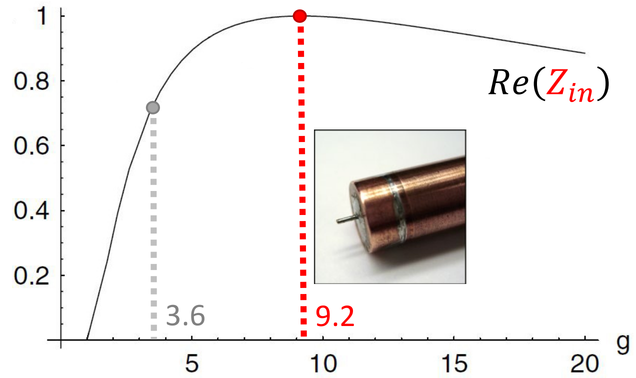
Coaxial cables with g = 3.6 (Z_0= *50 Ω or 75 Ω in air*) are made for ***traveling*** waves

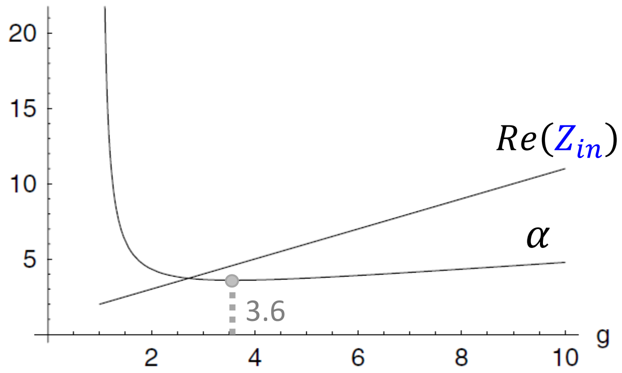
To serve as resonant trap, coaxial geometry must be optimized for ***standing*** waves

At ¹H frequency: $Re(Z_{in}) = \frac{\mu}{\pi}\sqrt{\frac{2\sigma\omega_H}{\varepsilon}} \cdot \frac{(\ln g)^2}{g+1} D$

At X frequency: $Re(Z_{in}) = lR_{surface} = \frac{\lambda_H}{4\pi}\sqrt{\frac{\mu\omega_X}{2\sigma}} \cdot \frac{g+1}{D}$

Maximum reflection at $g \approx 9.2$





Minimum loss with smaller g

Signal loss is lower when trap overall size is larger

Smaller g reduces trap loss at low-frequency at expense of higher ¹H losses

¹H-detection probes must have ¹H coaxial traps with g = 9.2: *Z_0 = 90 Ω for Teflon or Z_0 = 133 Ω for air dielectric*

^{1}H-Detect MAS probes

Homebuilt probes fit all three 800 magnets

800 MHz – 1.3 mm 60+ kHz

Advantages over Bruker HCN probe:

Tunable across wide isotope range ^{1}HXY:

^{103}Rh, ^{39}K, ^{14}N, ^{35}Cl…^{13}C…^{31}P (all but ^{19}F)

Materials + Biosolids

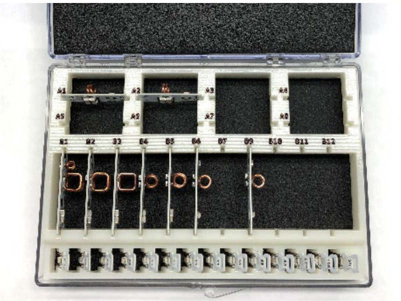
40-60% more ^{1}H S/N than in Bruker probe

Cools sample to 0°C

Homebuilt 1.3 mm spinner (W. Mao)

Easier to service in event of rotor crash

Will save $$ over time



In-house spinner parts

tunable across periodic table

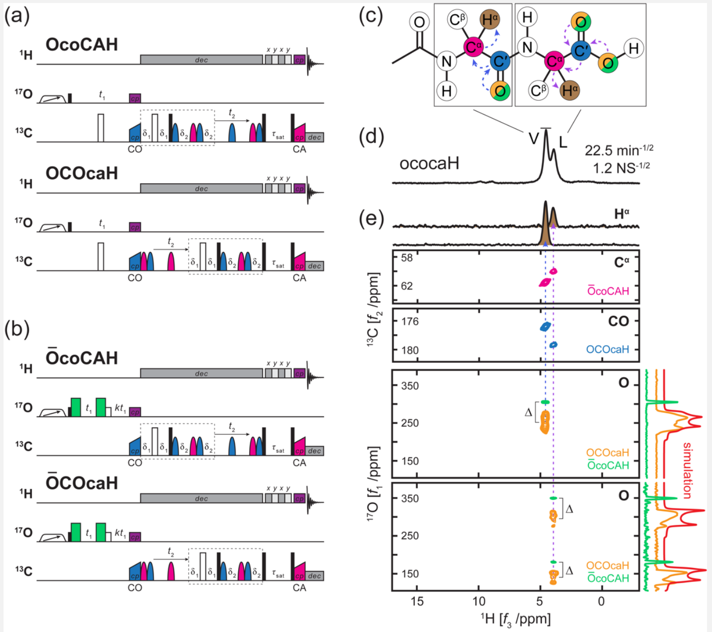
800 MHz – Ultrafast 100 kHz

0.75 mm JEOL spinner

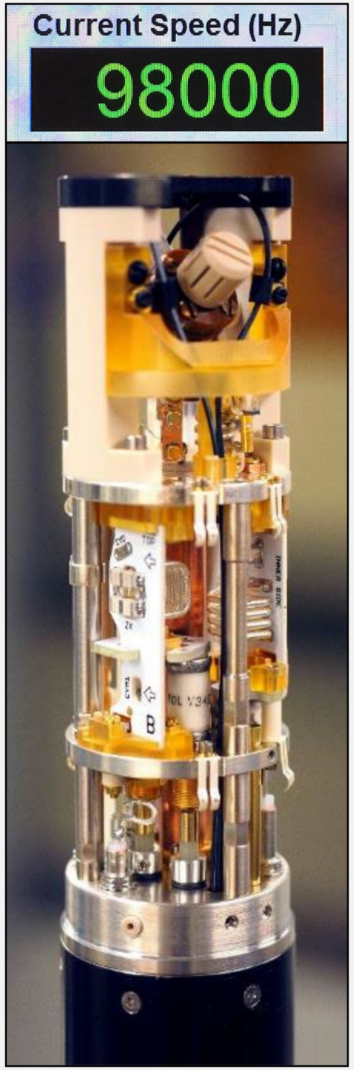
Circuit optimizes ^{1}H detection sensitivity

2X ^{1}H efficiency of commercial JEOL probe

Wide range of ^{1}HXY isotopes ^{25}Mg…^{31}P



^{1}H-detected 3-dim **^{1}H-^{13}C-^{17}O** correlation spectra of N-Ac-VL, 18.8 T, 90 kHz MAS. *Sample courtesy of Robert Griffin and Eric Keeler (MIT and NYSBC).*



Direct detection probes

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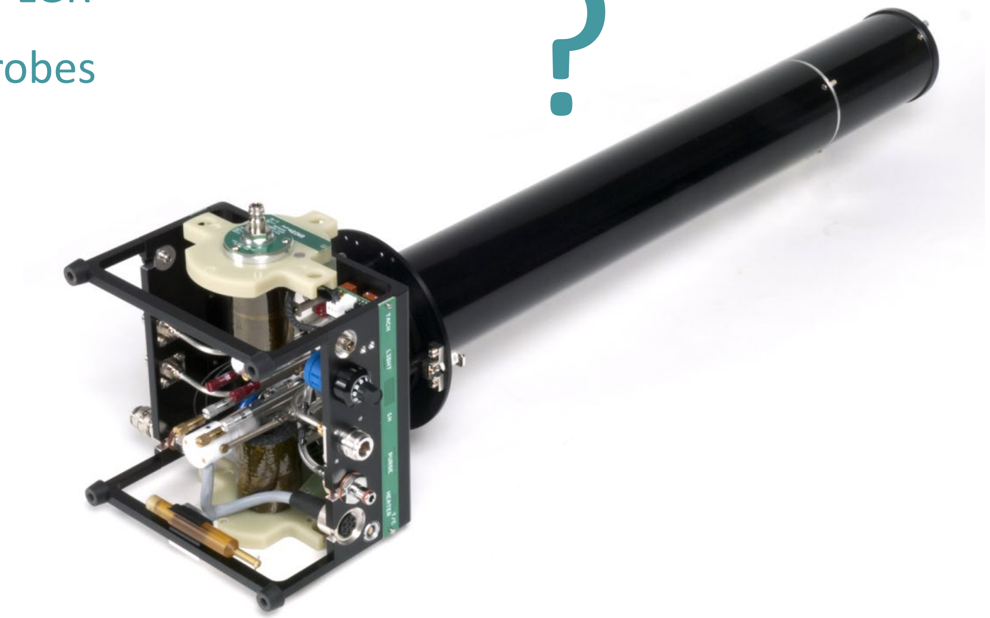
Double-CP experiments in biological samples

- Up to ~~900 MHz~~ 1.5 GHz
- Triple-resonance $^{1}H/X/Y$ (+^{2}H lock?)
- No sample heating from high power decoupling – as in scroll or LGR
- Best sensitivity of detection channel X (or Y) – as in solenoids
- Highest possible B_1 field homogeneity for CP – like in scroll or LGR
- Easy switch between different X and Y nuclei – as in Varian probes

  e.g. $^{13}C/^{15}N$, $^{13}C/^{2}H$, $^{31}P/^{13}C$, $^{31}P/^{15}N$….
- Optimize sensitivity either for X or Y detection
- Decent sample volume – e.g. 3.2 mm rotors

?



Two sample coils

^{1}H LGR outside

- Low ^{1}H *E* field – no decoupling heating in sample
- No ^{1}H wavelength effects in LGR – homogeneous B_1
- Tunable to higher fields and/or larger samples

X/Y detection solenoid inside

- Solenoid can have more turns
- Natural orthogonal isolation of ^{1}H signal
- No ^{1}H isolation traps to worry about
- Sensitivity boost for mid- and low-gamma detection

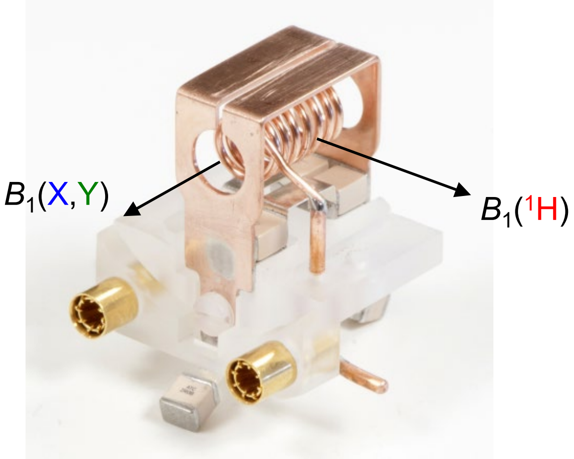
We call it ***Low-E***, others – ***loE*** or ***MAGiC***

Bruker calls it ***EFREE*** ™ – non-exclusive license from FSU

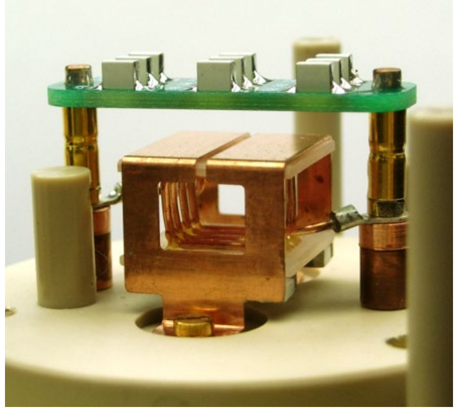
EFREE = "**E**lectric **F**ield **R**educed, **E**fficiency **E**nhanced"

Doty Scientific recently adapted similar design as ***BMAX***™

Check another cross-coil design by Doty called ***HMAX***™



3.2 mm MAS sample coils
(1st generation)
900 MHz

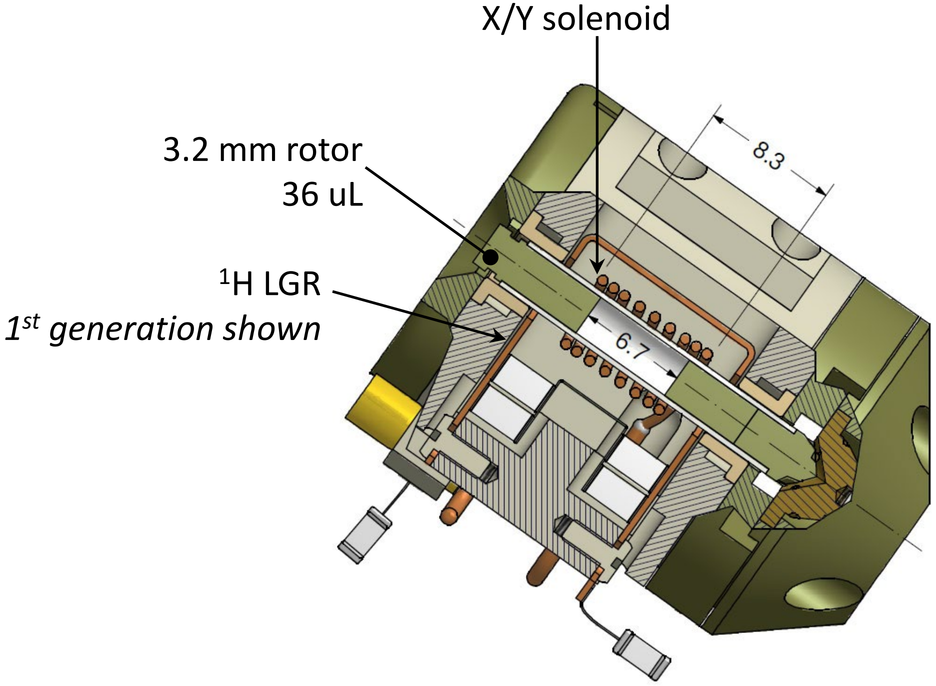


Large 500 µL coils for oriented protein samples
600-900 MHz
Gor'kov et al., JMR 2007

B_1 field homogeneity

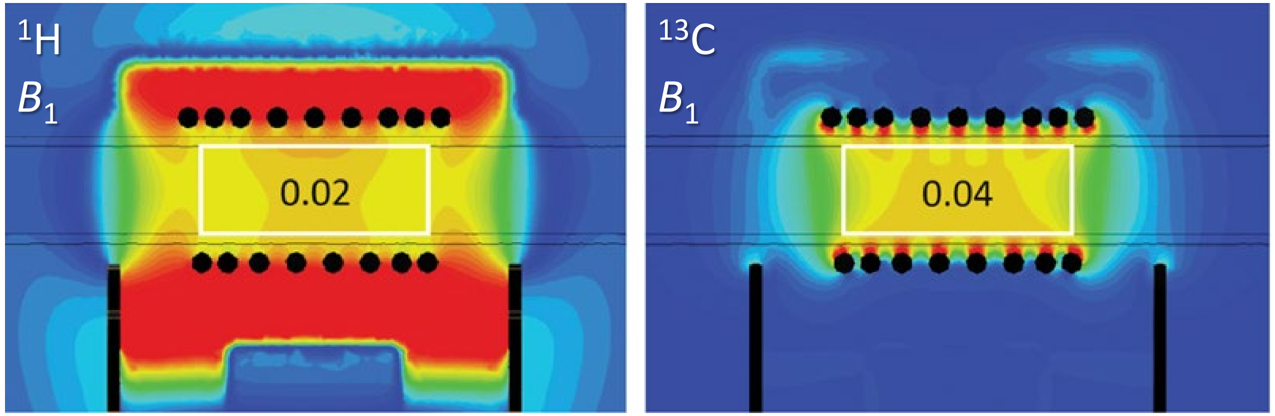
Rotor and spinner design considerations

- We custom-design spinners around coils
- Coils – around full available rotor volume
- Emphasis on homogeneous B_1 over max volume
- Detection coil has variable pitch



Nutation decay across full sample volume:
(from <u>900 MHz</u> ^{1}H/^{13}C/^{15}N probe)

^{1}H 810°/90° = 95%
^{13}C 810°/90° = 88%
^{15}N 810°/90° = 82%



<< Simulated B_1
^{1}H and X=^{13}C
600 MHz

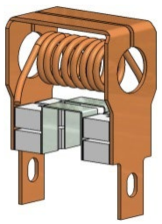
1st generation LGR
White rectangle is sample outline

Value in center = StD of B_1 across sample volume

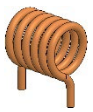
B_1 field homogeneity

Comparing to other probes using 3.2 mm Pencil rotor

^{1}H B_1 profile: X = ^{13}C B_1 profile:

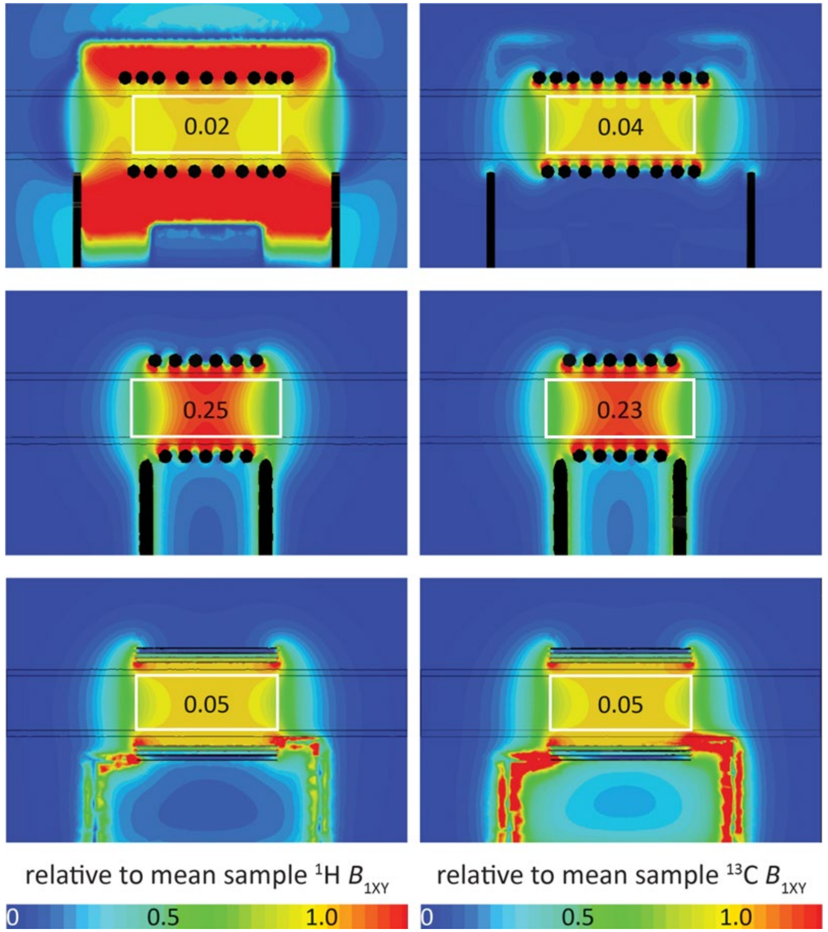


NHMFL
Low-E
1st gen.



Agilent
T3 Balun

Agilent
T3 Scroll



Simulated B_1 profiles at ^{1}H and ^{13}C frequencies, B_0 = 600 MHz.
White rectangle is sample outline in 3.2 mm 36 µL pencil rotor.
Center value = StD of B_1 across sample.

Direct detection pros and cons:

NHMFL Low-E:
- ✓ Best power efficiency at X/Y frequencies
- ✓ Good B_1 homogeneity and CP transfer

Agilent T3 Balun:
- ✓ Good power efficiency at X/Y frequencies
- ✗ Bad B_1 homogeneity and CP transfer

Agilent T3 Scroll:
- ✗ Poor power efficiency at X/Y frequencies
- ✓ Good B_1 homogeneity and CP transfer
- ✗ Detunes easily at high powers

Electric field and ^{1}H decoupling heating

Non-conservative ▯▯$E_1 \neq 0$ field is B_1-induced

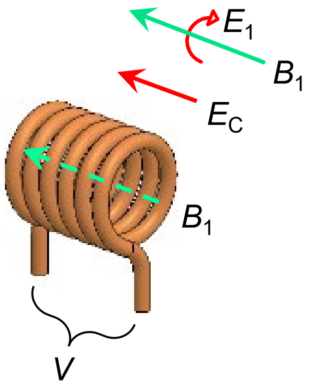
Conservative ▯▯$E_C = 0$ field is electrostatic

In solenoid $E_C \sim \omega LI/length \gg E_1$

High E_C/B_1 ratio heats bio samples

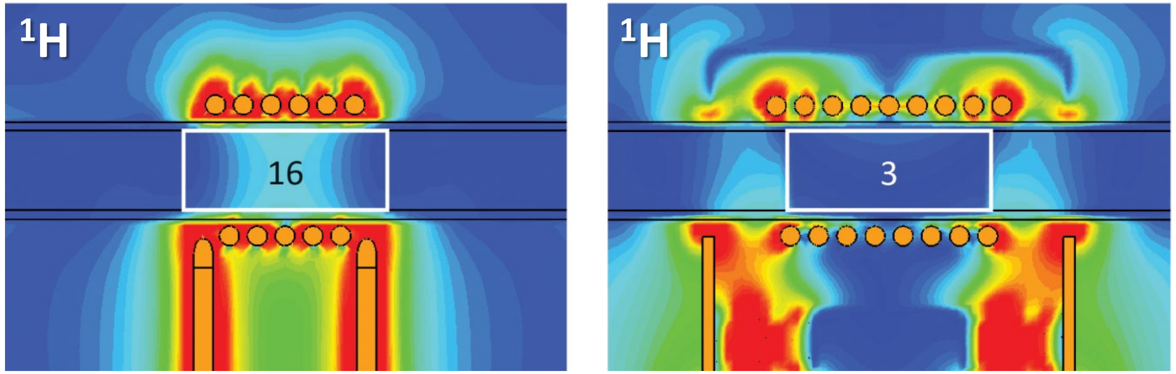
LGR has lower E_C/B_1 ratio

Inner solenoid is partial Faraday shield



E/B_1 in Solenoid

E/B_1 in Low-E coils



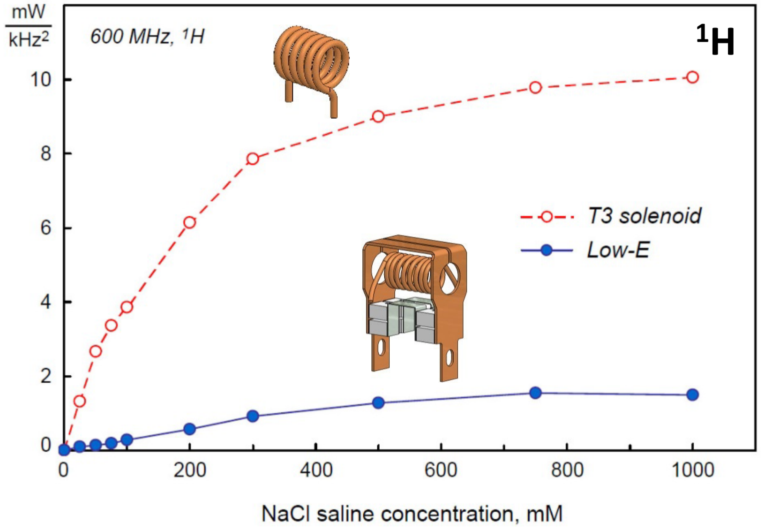
White rectangle is sample outline with sample-averaged E/B_1 value at 600 MHz

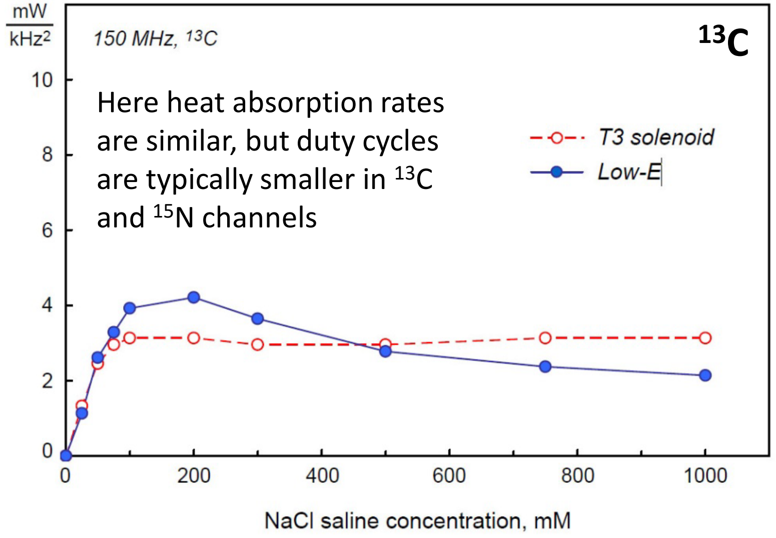
Measured heat absorption rate in saline samples, Watt per kHz^2 of *nutation rate* f_1:

$$q_{HEAT} = \left(\frac{Q_{NL}}{Q_{BIO}} - 1\right) \cdot \frac{P_{INPUT}}{f_1^2}$$

Q_{NL} and Q_{BIO} = probe Q's with non-lossy and biological samples

Heat absorption in conductive samples, per $(\omega_1/2\pi)^2$





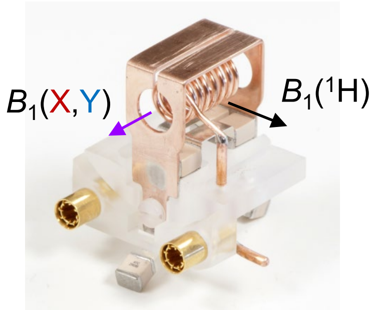
3-resonance ^{1}H–X–Y circuit

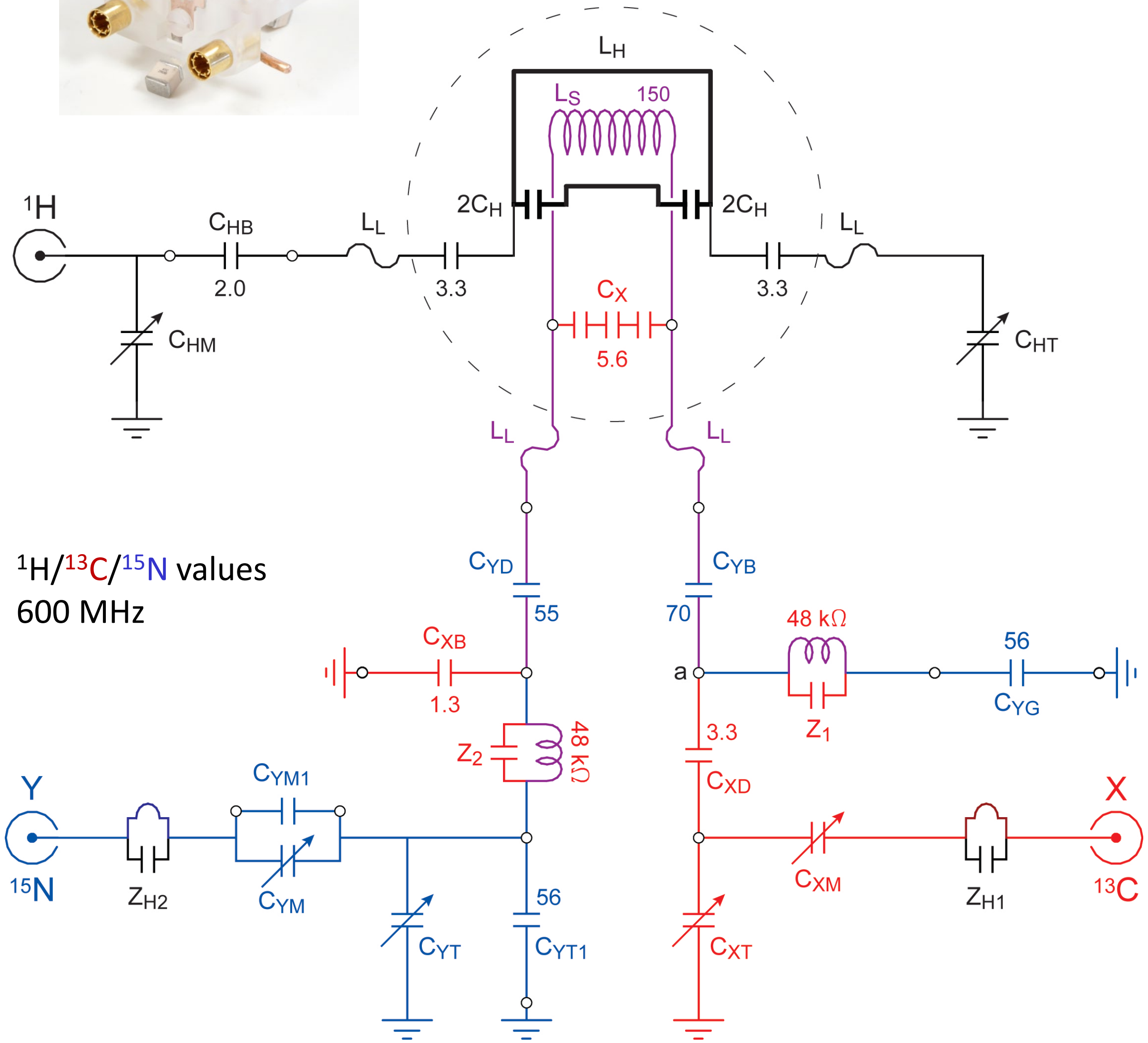
With Low-E cross coils

- ^{1}H channel is separate 1-resonance circuit
- Solenoid is double-tuned to X/Y, resonated above ω_X
- Isolation from ^{1}H to X/Y is 30…50 dB
- Electrically balanced on all 3 channels
- Middle channel X is easy to balance
- Balancing is typically done to reduce voltages (arcing)
- Allows us to use smaller tuning trimmers

Note that

- Most folks would not balance middle channel X
- Because balancing X requires extra resonant trap
- Which is believed to add extra loss…
- Here the effect is opposite!





^{1}H/^{13}C/^{15}N values
600 MHz

Balanced detection channel = more S/N

Cost of Adding 3rd channel Y

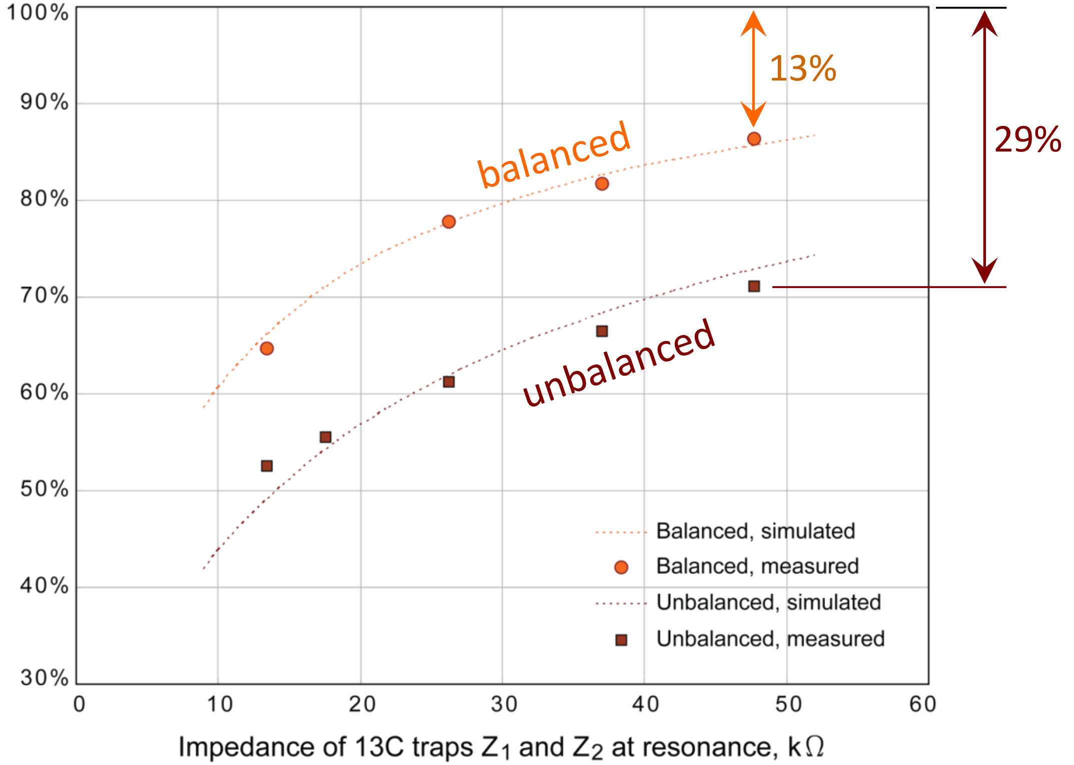
$$\frac{^{13}C \text{ S/N 3-resonance}}{^{13}C \text{ S/N 2-resonance}}$$

Balanced ^{13}C channel
Two ^{13}C traps


+


versus

Unbalanced ^{13}C channel
One ^{13}C trap



→ *Different L-C trap geometries* →

- Balancing middle detection channel X with additional lossy trap = higher S/N, counterintuitively

Optimize L-C trap for ^{13}C detection

Signal loss in isolation traps varies on ***geometry***

Loss in L-C reflection trap at ^{13}C detection freq-cy ω_X:

$$P_{loss}(\omega_X) = \frac{V^2}{Re\,Z\,(\omega_X)} \qquad Re\,Z\,(\omega_X) = \omega_X \boldsymbol{LQ}$$

Goal is to maximize $\boldsymbol{LQ}$

Measure trap impedances $\boldsymbol{LQ}$ – not just trap Q

We use traps with $Re\,Z\,(\omega_X) \geq 50\ \mathrm{k\Omega}$ *

Chip capacitor ***orientation*** matters:

- Eddy currents in chip plates reduce trap $\boldsymbol{Q}$

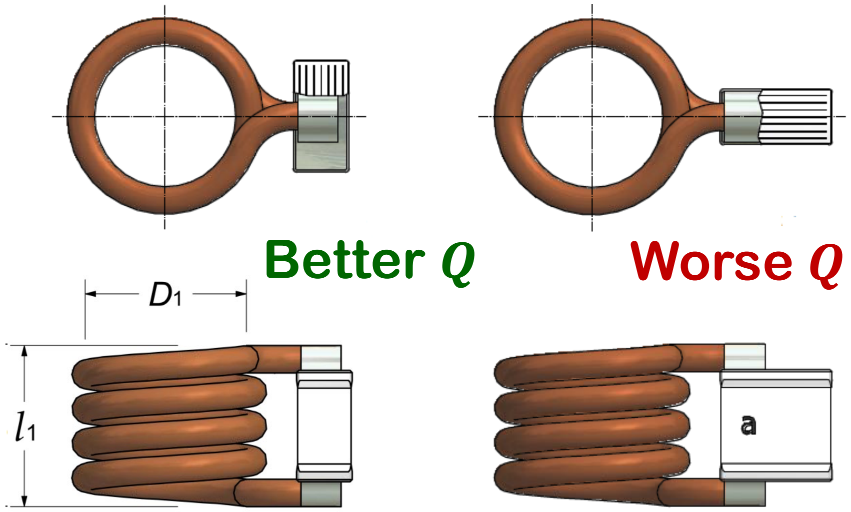
Physical boundaries constraints:

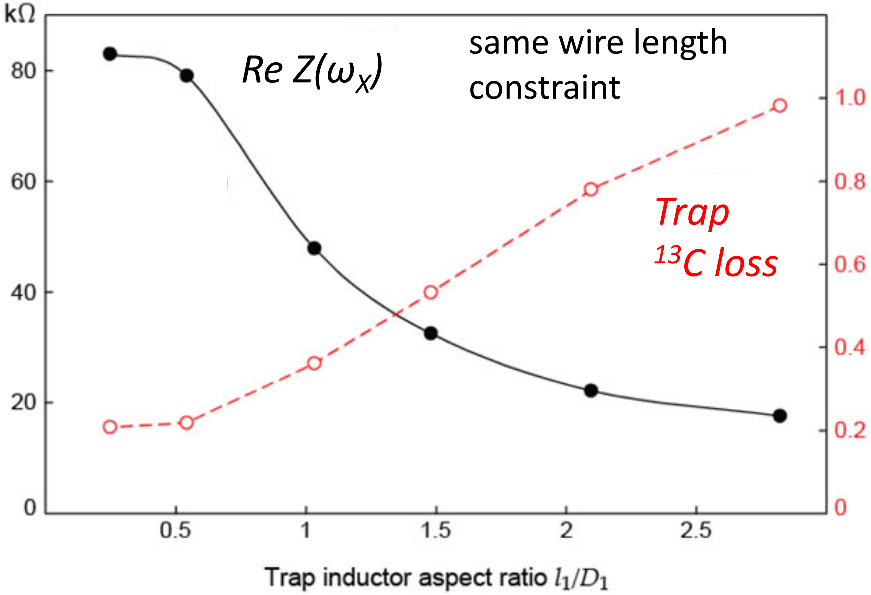
- ***Rectangular*** trap section increases $\boldsymbol{L}$ →

^{15}N loss constraint = same wire length and dia:

- ***Shorter*** aspect ratio l_1/D_1 increases $\boldsymbol{LQ}$


3D printed Cu traps





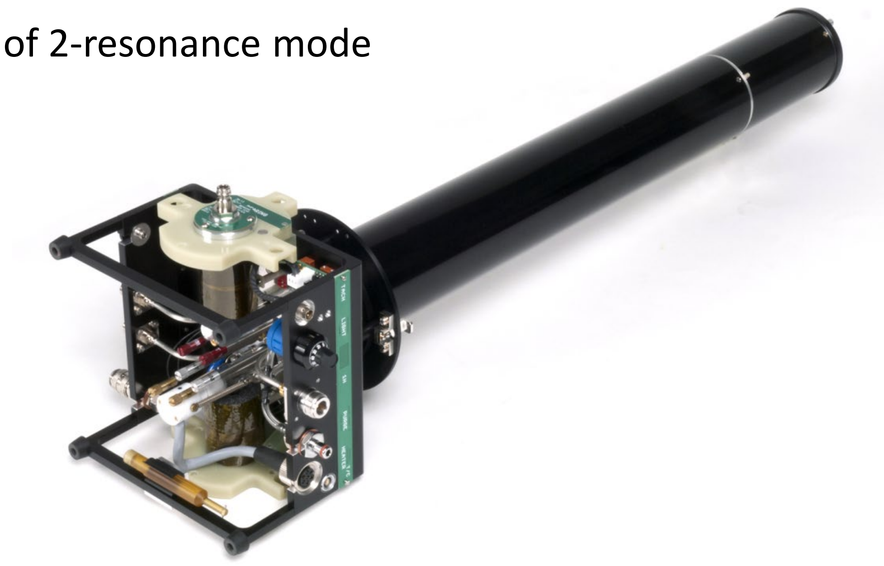
"LEGO" probe frame for WB magnets

- Designed for quick replacement of every component, "LEGO" style
- C-size NP0 chips with silver terminal plates
- Quickly switch X and Y isotopes:

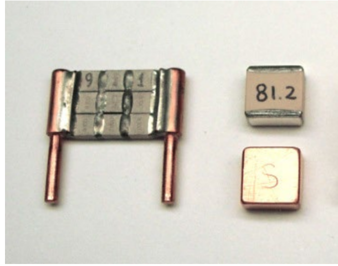
  X/Y = $^{13}C/^{15}N$, $^{13}C/^{2}H$, $^{31}P/^{13}C$, $^{31}P/^{15}N$ ...
- Chose optimal isolation trap geometry for

  X detection

  Y detection
- Choice of 2-resonance mode



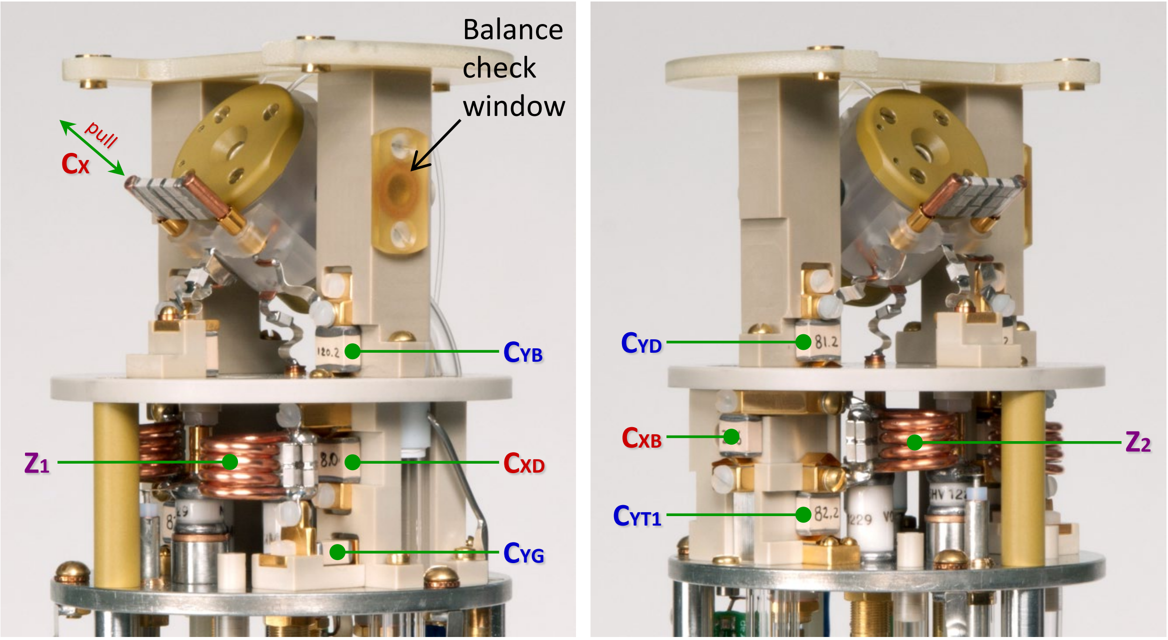
"LEGO" blocks



Caps and shorts

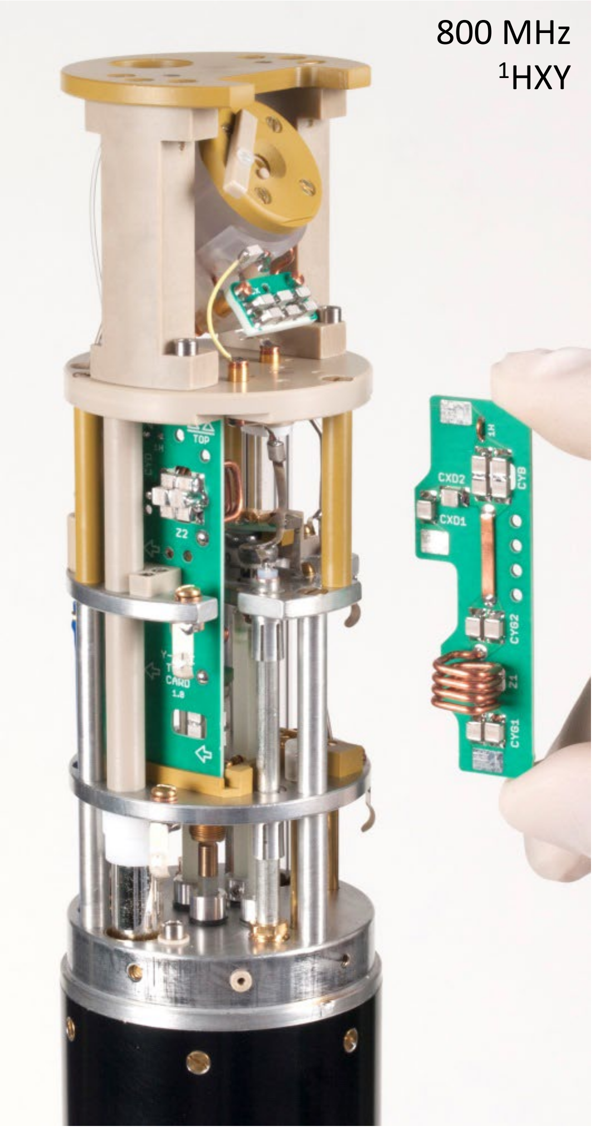
X optimized trap

Y optimized trap



3-resonance RF circuit layout

Tune cards for smaller magnet bores

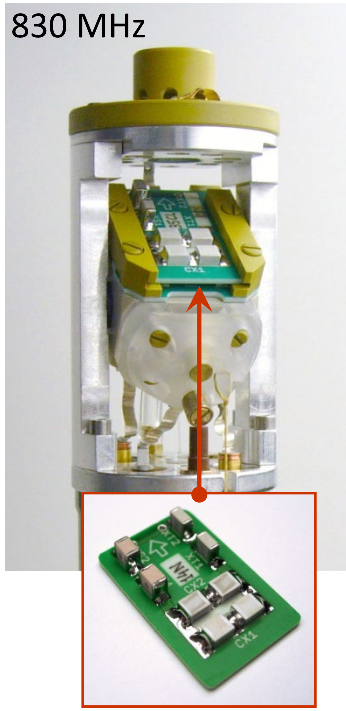


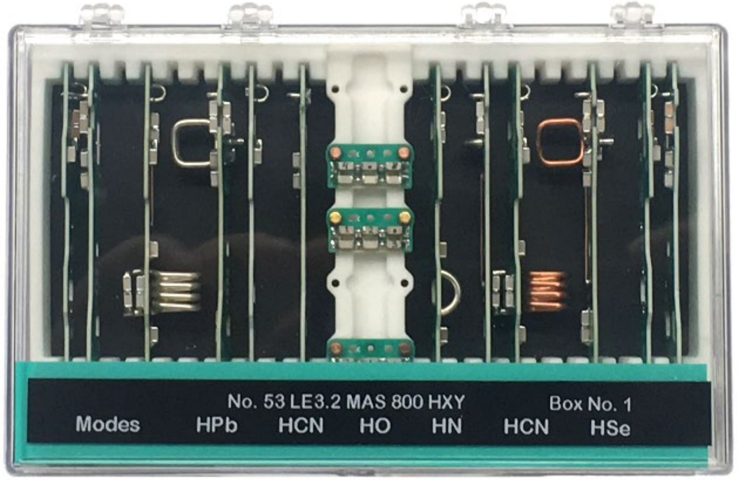
Inspired by SIM card mechanics found in older cell phones

Two cards slide into the probe to set desired **X** and **Y** isotopes

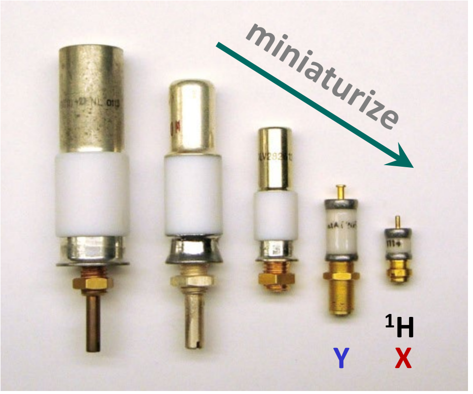
Trap geometry is varied to **optimize S/N** for detection in **X** or **Y** channels

Cards are made of low-loss microwave substrate





Most RF circuitry is mounted on cards except for tune and match trimmers



Smarter RF circuit layout removes bulky high voltage components while maintaining power handling

830 MHz
bore size
= **31** mm

Making ^{1}H LGR for 1.5 GHz

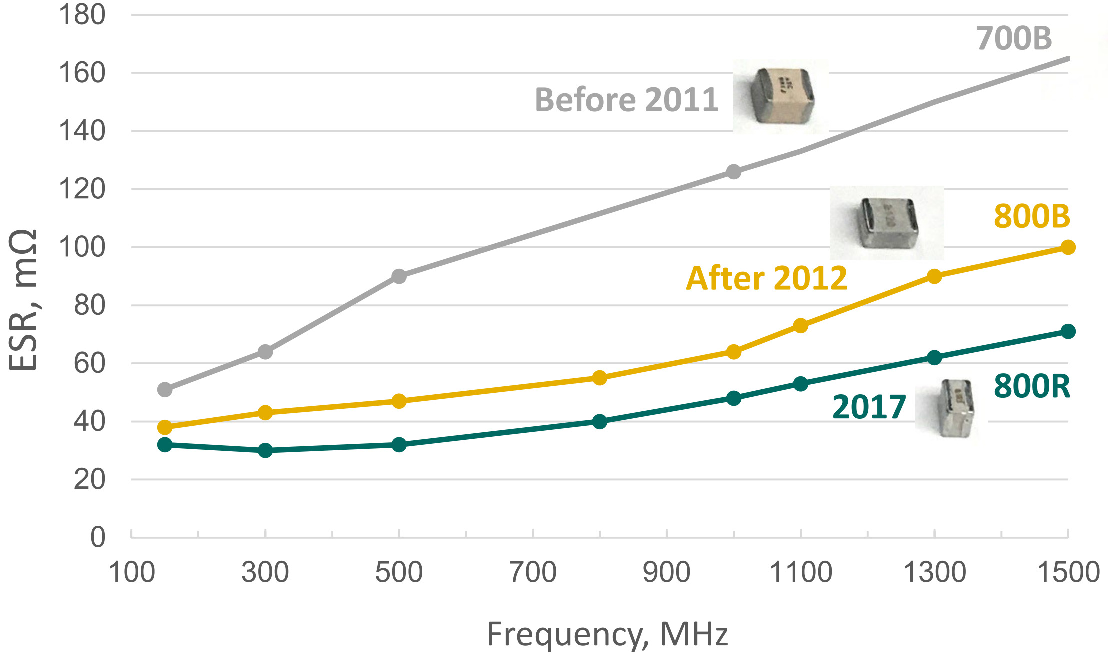
Challenges

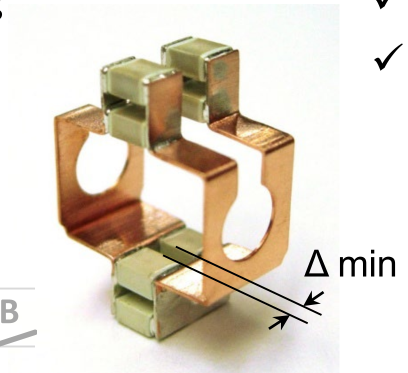
- × RF loss in ceramic chips increases with ^{1}H frequency
- × Degrades ^{1}H power efficiency
- × May overheat, detune, crack during long decoupling

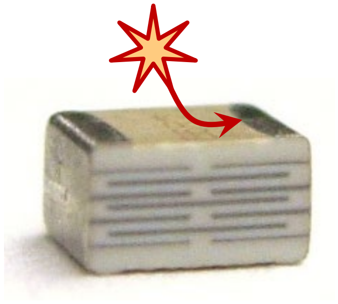
Solutions

- ✓ **New low-loss ceramic chips since 2017**
- ✓ Parallelizing chips reduces overheating
- ✓ Route spinner exhaust gases to cool LGR chips
- ✓ Use **NP0** temperature-compensated ceramic

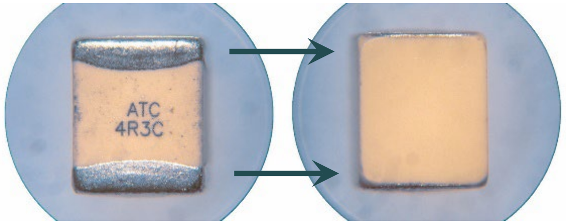
Advances in high-power non-magnetic chips
American Technical Ceramics

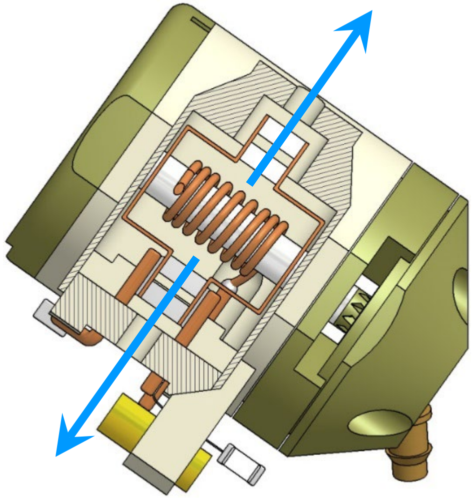






remove chip terminal edges





Spinner **exhaust** is designed to flow gas around LGR chips

3.2 mm MAS Probes at 1.5 GHz

Need new detection coils ≥ 1.2 GHz

3.2 mm is large volume coil for 1.2 and 1.5 GHz

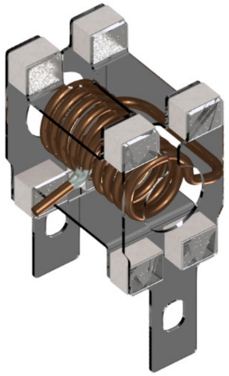
Circuit voltage □B_0 for same nutation rate

At 1.5 GHz f (^{13}C) = 377 MHz !

Hard to tune ^{13}C…^{11}B range without reduction in S/N

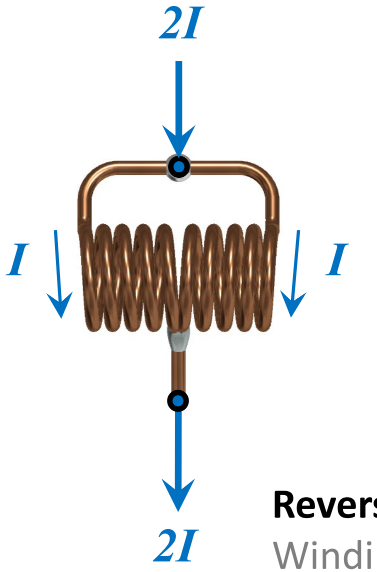
Sample dielectric loss at detection frequency

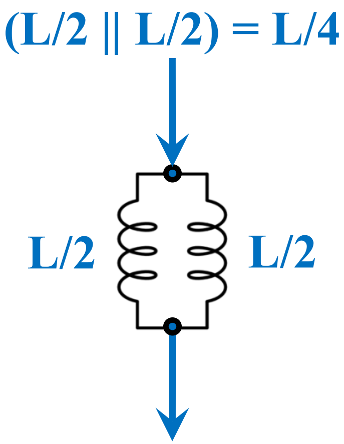
1.5 GHz variation on
US9411028B2 (2016)
Zhang, Fey, Gor'kov



Reverse-wound solenoid + LGR

- ✓ Same B_1 field profile as in straight solenoid
- ✓ Lower inductance
- ✓ Higher B_1 without arcing
- ✓ Lower electric field
- ✓ Better sensitivity for $\omega_X \geq {}^{13}$C… (mid-γ)
- ✓ 25% more S/N in biological samples
- ✓ Higher RF fields





Reverse-Wound Solenoid
Winding direction reverses in the middle
End turns are soldered to each other

1.5 GHz 3.2 mm ^{1}HX
middle-gamma MAS probe
Materials + Biosolids

Additional Comments:

Above 1 GHz, we need new RF detection coils to overcome several problems.

Voltage in RF circuit grows linearly with B_0 field. At 1.5 GHz arcing is a cause of insufficient decoupling in probes with larger samples like 3.2 mm.

Also, many interesting nuclei reside in 300-500 MHz range. Using conventional solenoid to detect at these frequencies can adversely affect sensitivity even when cross-coil designs are utilized.

Instead, for detection, we use reverse-wound solenoid with same B1 distribution as in normal solenoid, only its winding direction is reversed in the middle while its ends are joined.

Such coil has much lower inductance and can reach higher B_1 field without arcing.

In biological experiments on lossy samples such coil can be 25% more sensitive than normal solenoid.

The loop-gap resonator responsible for ^{1}H decoupling was also redesigned to withstand higher voltages. We now safely reach at least 82 kHz decoupling at 1.5 GHz field.

(last slide) Thank you!