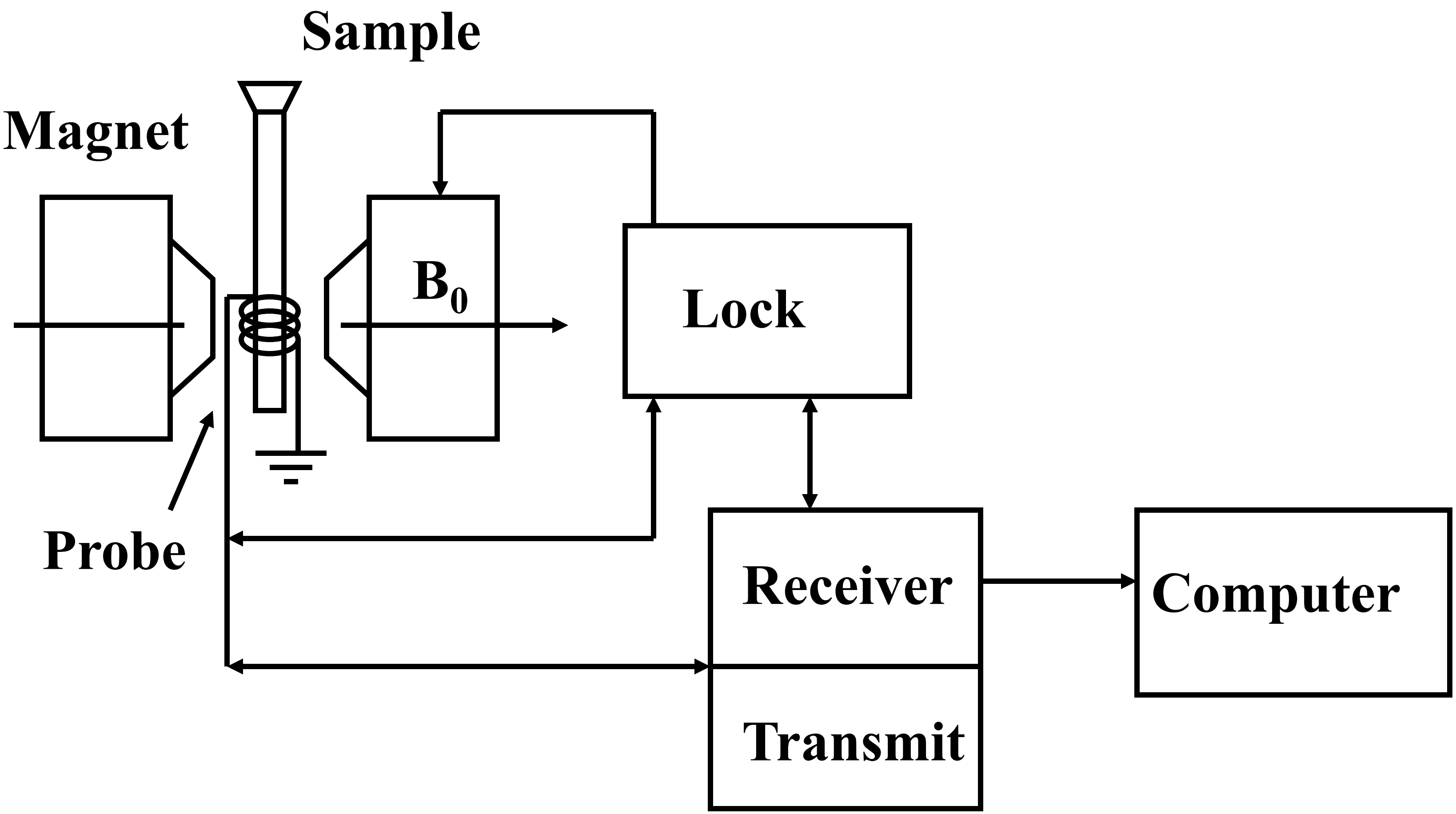
NMR Instrumentation

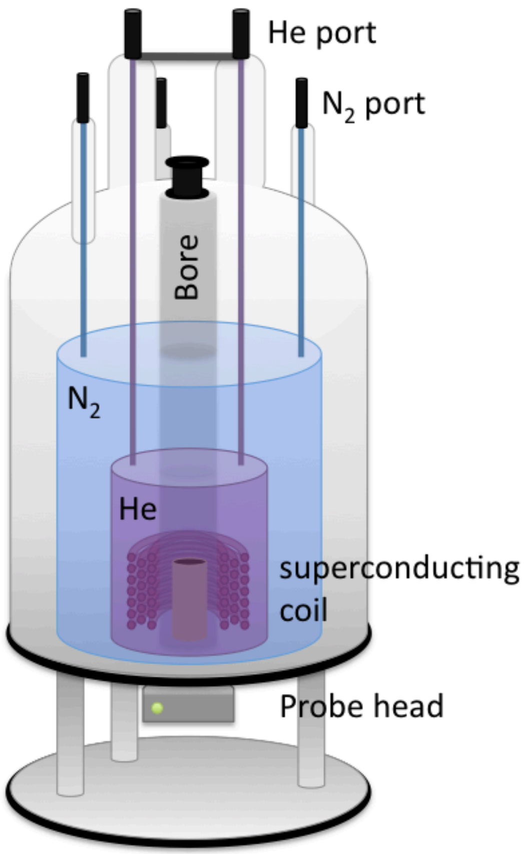
BCMB/CHEM 8190

Biomolecular NMR

Instrumental Considerations - Block Diagram of an NMR Spectrometer



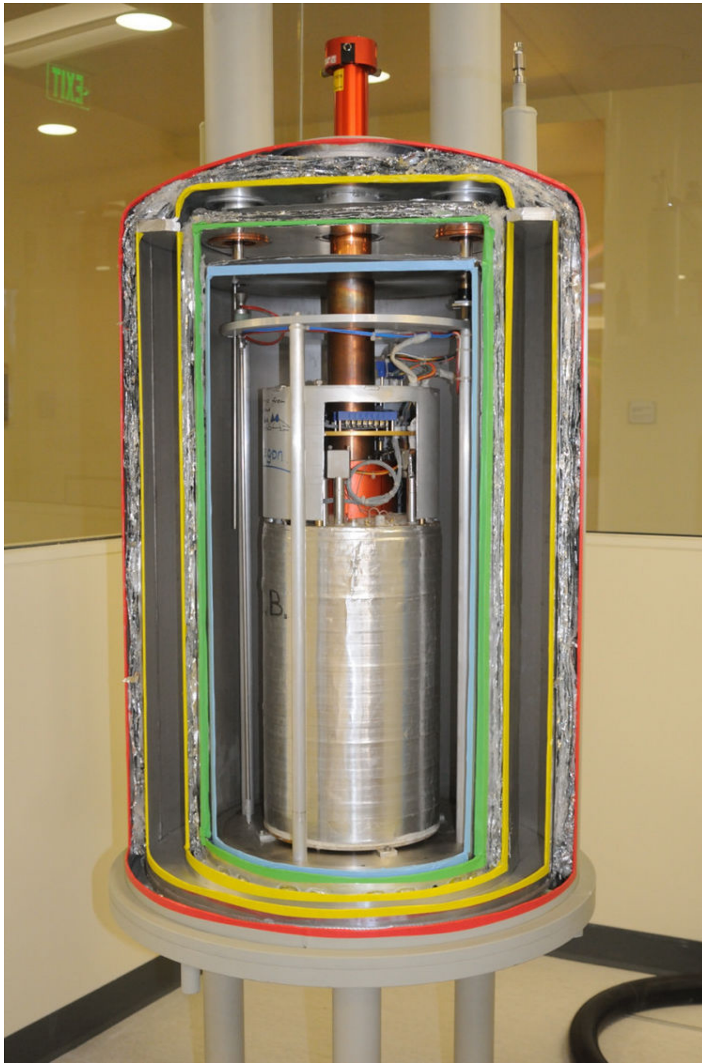
Superconducting Magnet systems



24.0 T (1020 MHz) magnet system (NIMS, Japan)

From the outside:

1. **Red** (outer shell)
2. Mylar insulation
3. **Yellow**, liquid N_2 Dewar
4. Mylar insulation
5. **Green**, heat shield
6. **Blue**, liquid He Dewar
7. Superconducting coil (wrapped in silver tape)
8. Copper bore tube (through center of magnet

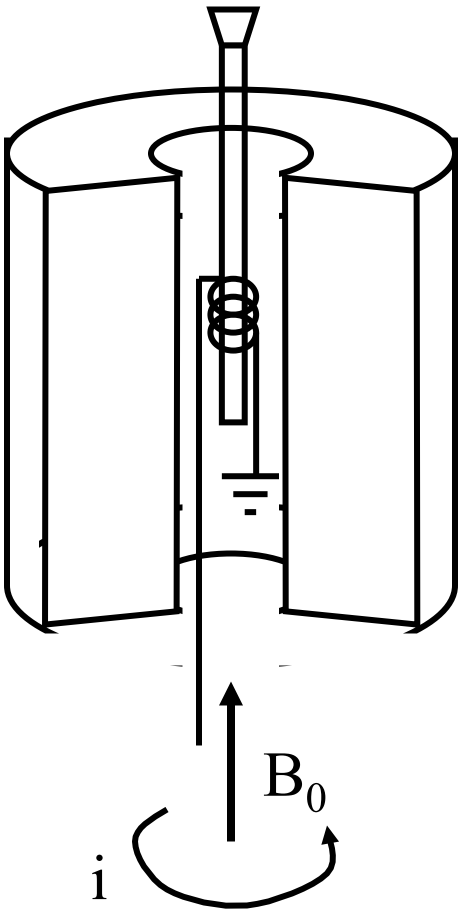


https://www.chemie.uni-hamburg.de/nmr/insensitive/tutorial/en.lproj/spectrometer.html

https://nmr.science.oregonstate.edu/index.php/Cross-section

https://www.sciencedaily.com/releases/2015/07/150702184036.htm

Modern NMR Magnets are Superconducting Solenoids



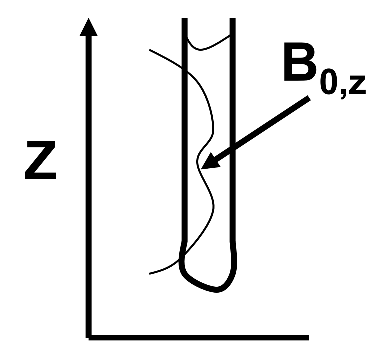
- Advantages:
  - -high field
  - -stability
  - -homogeneity > 1 : 10^9

- Materials: NbTi < 10T, NbSn > 10T
- Max Field (2015): 24.0 T (1020 MHz)
- New HTS alloys (2017?): ~35T (~1.5 GHz)
- Hybrid magnets: 45T **

**https://nationalmaglab.org/about/around-the-lab/meet-the-magnets/meet-the-45-tesla-hybrid-magnet

Magnetic Field Homogeneity

- In a perfectly homogenous magnetic field, all nuclei in a sample would experience the same effective magnetic field strength
- In such a case, the Larmor frequencies would be identical ($\upsilon_0 = -\gamma B_0/[2\pi]$), and linewidths "infinitely" narrow
- We can calculate what an acceptable variation might be
  - example: for a ^{1}H at 600 MHz (14.09 T) and a maximum allowable difference in υ_0 ($\Delta\upsilon_0$) of 0.1 Hz, the maximum change in field strength (ΔB_0) is $\Delta B_0 = 0.1(2\pi)/\gamma = 2.4\times10^{-9}$ T, or 1.7×10^{-10} of B_0 !
- The magnets themselves do not achieve this level of homogeneity
- To achieve high resolution, small adjustments must be made to the main magnetic field to improve its homogeneity

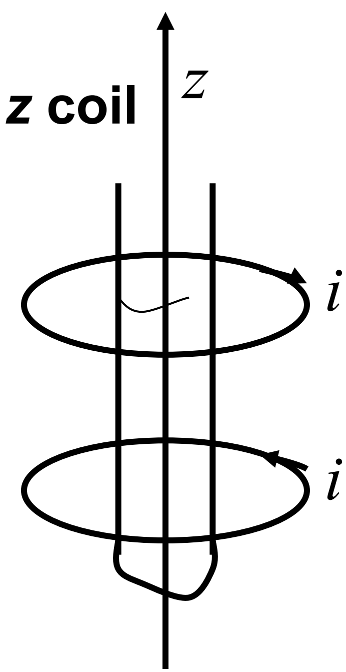


Solution: shim coils, shimming

- The magnetic field homogeneity can be improved through a process known as "shimming" (term comes from "shim stock", small pieces of metal used to adjust position and orientation of pole pieces in old electromagnetics to improve homogeneity)

- Modern magnet systems include "shim coils", sets (16-40) of wire coils placed judiciously around the sample to allow adjustments to the magnetic field at the sample by *adjusting the current in the coils*

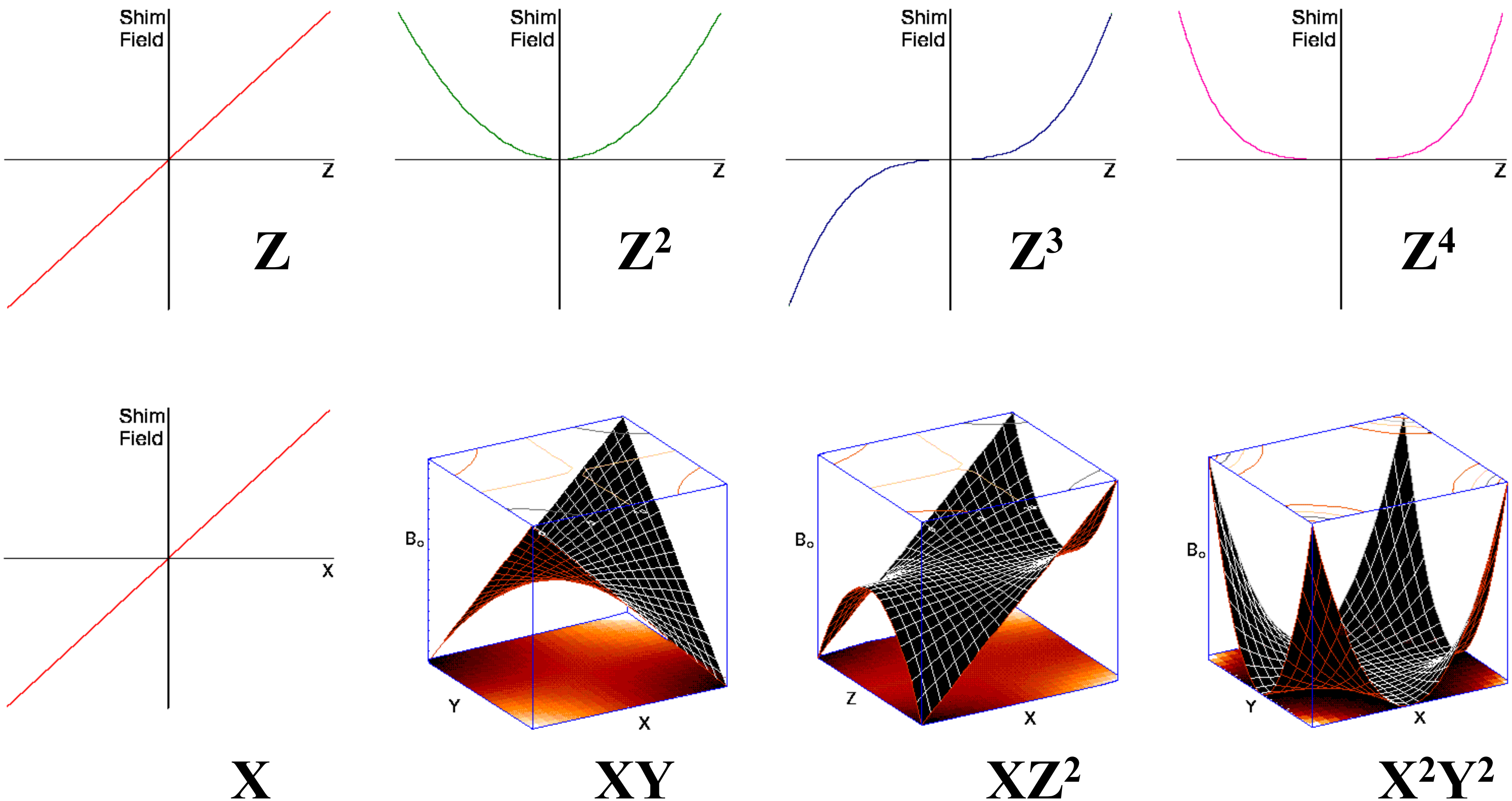
a linear z coil



- Consider the B_0 field profile as a power series: $B_0(z)=B_0+a1z+a2z^2+\ldots$
- Design shim coils to compensate ($-a1z, -a2z^2$, ...)
- Also x, y, powers, cross terms, etc.

Solution: shim coils, shimming

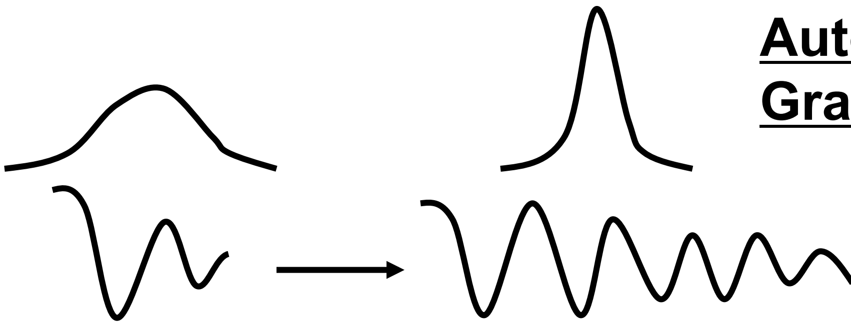
- A set of 40 shim coils then provides a mechanism to make very delicate and precise adjustments to the magnetic field shape, and thus the homogeneity



From *The Basics of NMR*, Joseph P. Hornak

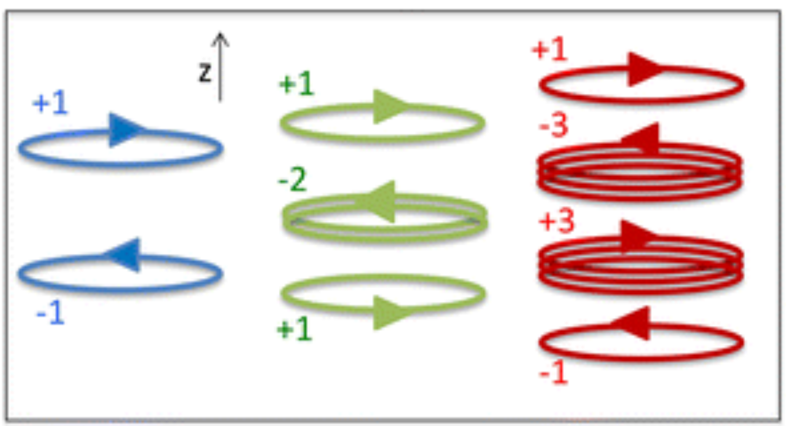
Shimming

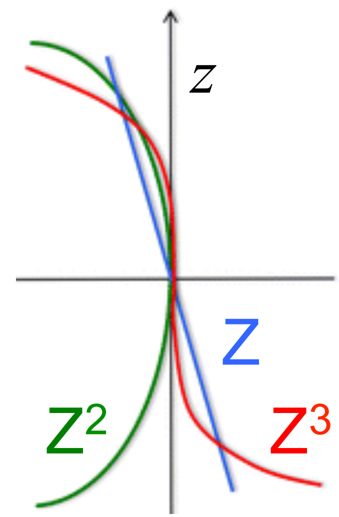
- Shimming improves peak width and S/N (increase homogeneity decrease T_2^* relaxation) and improves peak shape



<u>Auto shim</u>: based on lock signal amplitude

<u>Gradient shim</u>: observe effect of imposed field gradient – deconvolute field inhomogeniety

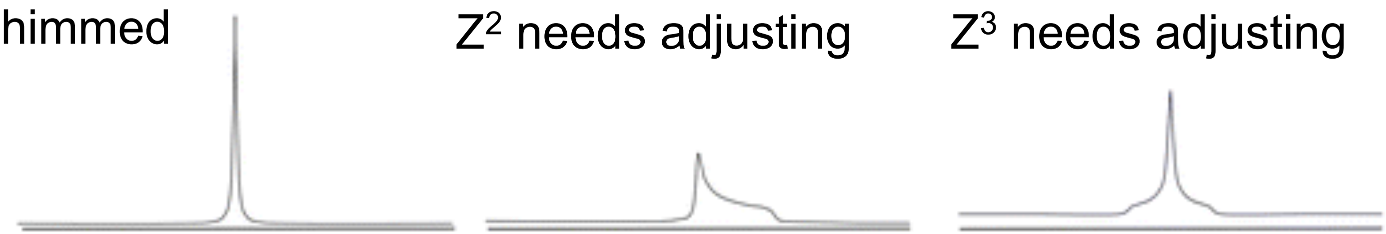




well shimmed

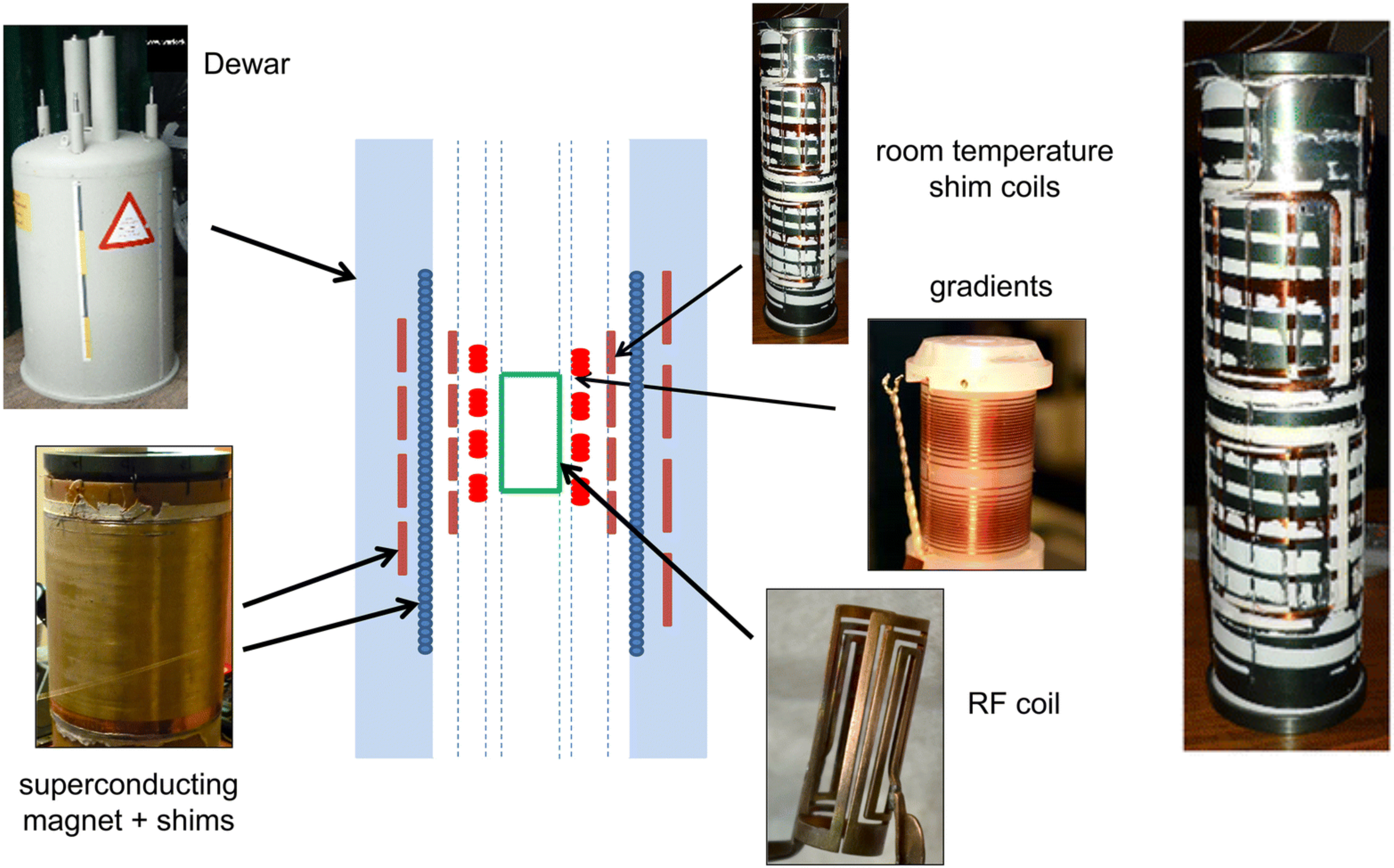
Z^2 needs adjusting

Z^3 needs adjusting



http://pubs.rsc.org/is/content/chapterhtml/2016/bk9781782623595-00001?isbn=978-1-78262-359-5&sercode=bk#sect866

Shim Coils

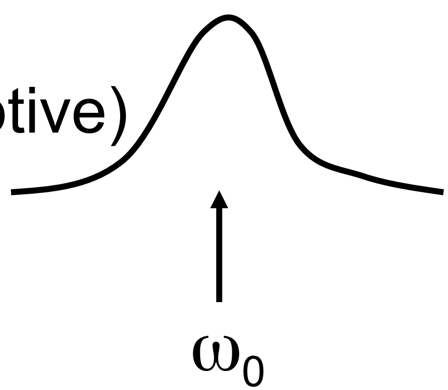


http://pubs.rsc.org/services/images/RSCpubs.ePlatform.Service.FreeContent.ImageService.svc/ImageService/ChapterImage/bk9781782623595/BK9781782623595-00001/bk9781782623595-00001-f2_hi-res.gif

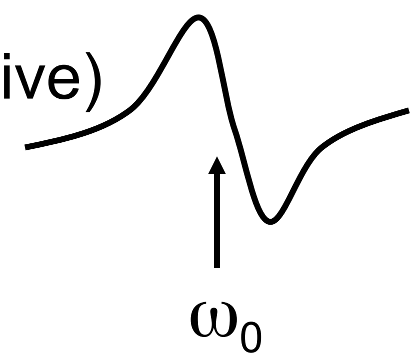
A Deuterium Lock Stabilizes the Field

- The field strength of a typical high field NMR magnet will change, or "drift", by a few Hz per hour
- The "lock", or *field-frequency locking system* adjusts the magnetic field to compensate for this drift

X axis
(absorptive)

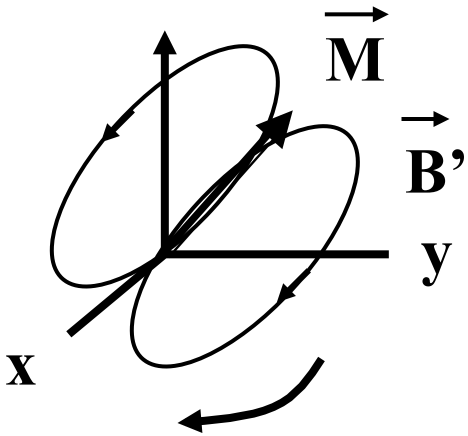


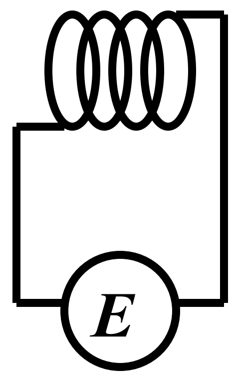
Y axis
(dispersive)



Drift of field will produce positive and negative signals
Depending on direction when dispersive signal is observed

Detection of NMR Signals: Probe Coils



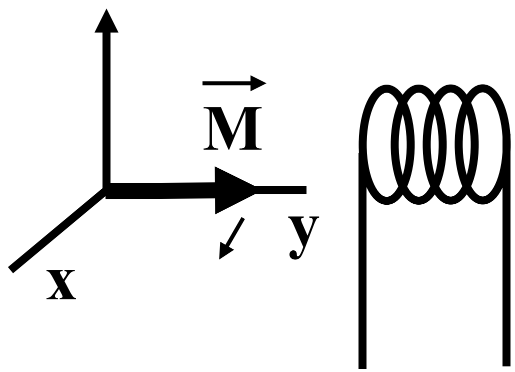


$$E \propto dB'/dt \propto dM/dt \propto \gamma B_0 M_0 = N\gamma^3 B_0^2 \hbar^2 I(I+1) / (3k_B T)$$

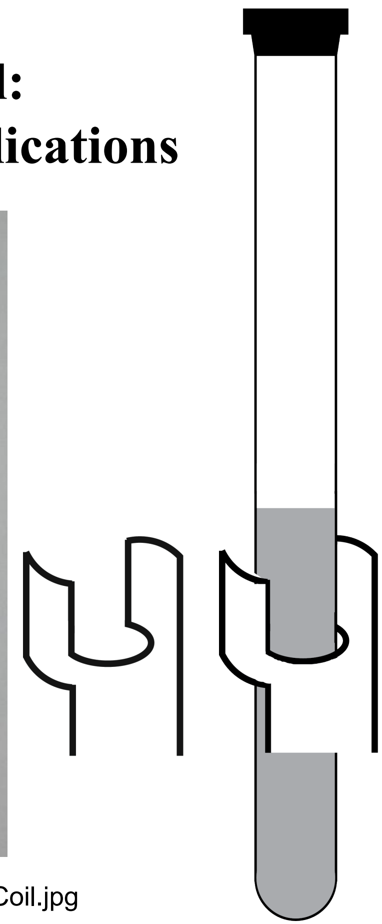
$$S/N \propto (\gamma_C / \gamma_H)^3 = 64^{-1}$$

Probe Coils

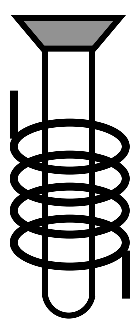
- The probe coil serves a dual role:
  - -to deliver the B_1 field pulse to the sample
  - -and to detect the oscillating bulk magnetization (dM_y/dt)
- The coil is orientated *perpendicular* to B_0



Helmoltz coil:
-normal applications



solenoid coil:
-specialized applications



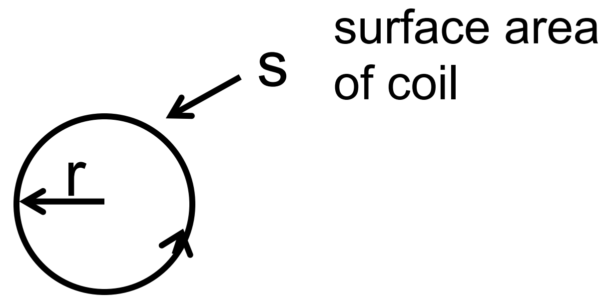
https://nmr.science.oregonstate.edu/index.php/File:Coil.jpg

Coil Design: Needs/Implications

Requirements: 1). Maximize B_1 from applied rf current
2). Maximize signal (S) from $\vec{M}$ of sample

look at 2

$$\mathbf{S} \propto \frac{d\vec{\mathbf{B}}'}{dt} \times \vec{\mathbf{s}}$$



$$\mathbf{B}' \propto \frac{\mathbf{M}}{\mathbf{r}^3} \qquad \mathbf{s} \propto \mathbf{r}^2$$

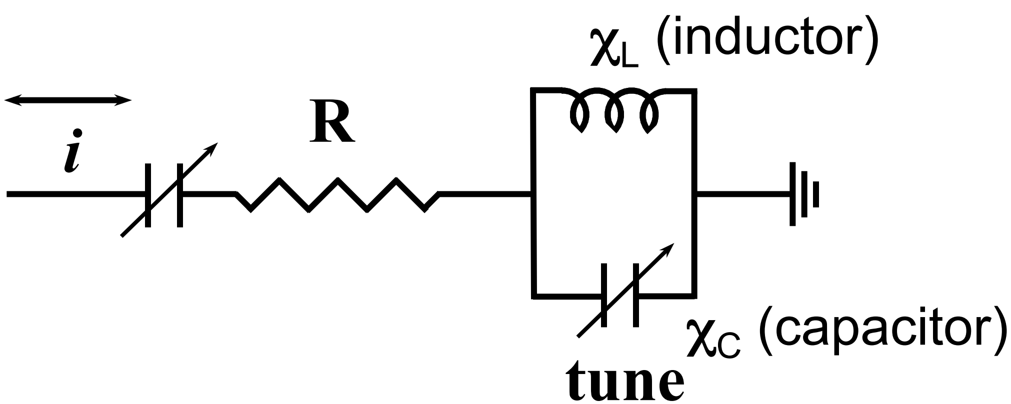
$$\mathbf{S} \propto \frac{\mathbf{M}}{\mathbf{r}}$$

So:

-minimize coil size to increase S
-maximize sample volume to increase M
-these demands conflict one another
(compromise)

Tuned Radiofrequency Resonance Circuits Improve Efficiency

- Proper dissipation of the RF pulse to the sample requires the impedance of the circuit (which includes the rf coil *and* the sample) must be equal to that of the transmitter and the receiver
- Impedance is adjusted to a 50 Ω resistive load (no reactance)
  - example: parallel LC (inductance/capacitance) circuit



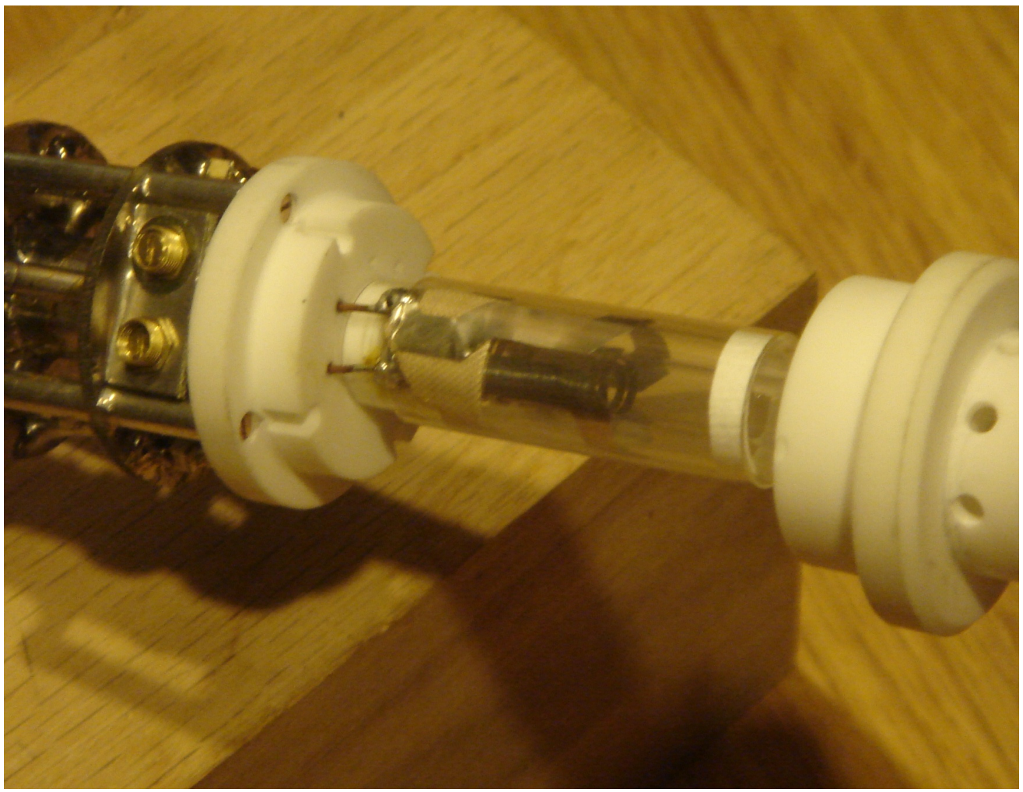
Impedance (Z): total opposition to current flow
Reactance (χ): opposition to current flow caused by inductance and capacitance but not resistance
Inductance (L): property of an electric circuit by which an electromotive force is induced in it as the result of a changing magnetic flux
Capacitance (C): ratio of charge to potential (ability to store charge)

- complex impedance: $Z = R + i\,(\chi_L - \chi_C)$, $\chi_L = 2\pi\nu_0 L$, $\chi_C = 1/(2\pi\nu_0 C)$
- the circuit is resonant ("tuned") when the impedance is purely resistive ($\chi_L = \chi_C$)
- the tuned resonance frequency $\equiv \upsilon_0 = \dfrac{1}{2\pi\sqrt{LC}}$

What does an NMR Probe Look Like?

This is for a 7T magnet – ^{13}C observe at 75 MHz

Probes are delicate – glass, teflon, ceramic, electronics

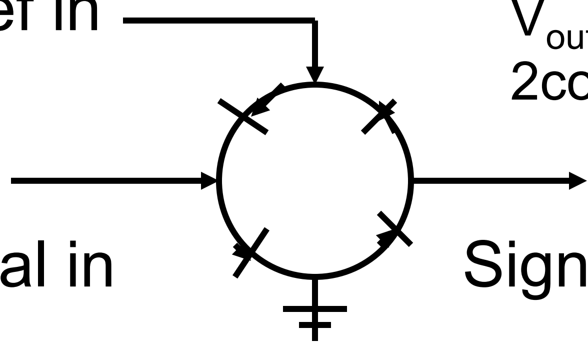


https://nmr.science.oregonstate.edu/index.php/File:Coilelectronic.jpg

Receiver Functions

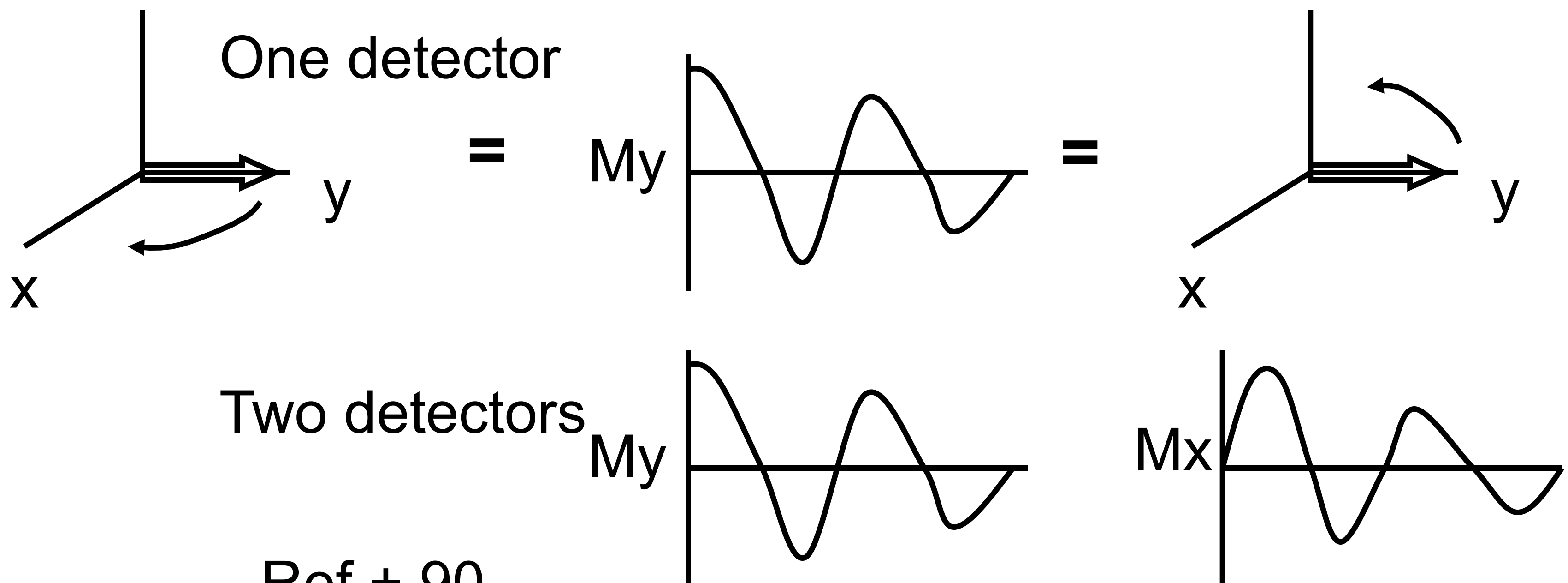
1. Amplify signals: 10 microV $\longrightarrow$ 1 V
   Three stages 30 dB/stage
   dB = 10 x log(P_{out}/P_{in}) = 20 x log (V_{out}/V_{in})

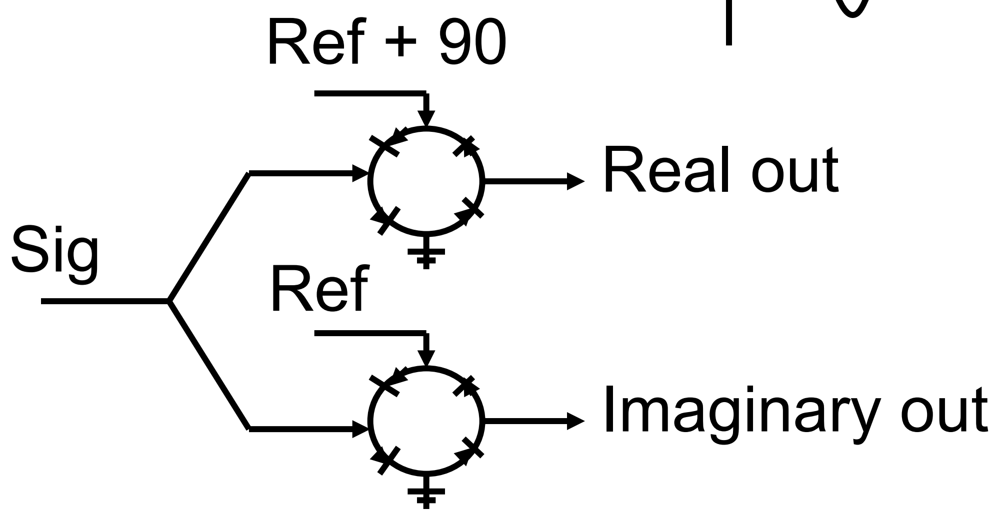
2. Shift Frequency: 100 MHz -> 1 KHz
   convenient digitization in the “rotating” frame
   often uses a “double-balanced mixer”



$V_{out} = a_0V_{in} + a_1V_{in}^2 + \ldots$
$2\cos(\omega s)\cos(\omega r) = \cos(\omega s\text{-}\omega r) + \cos(\omega s+\omega r)$

Quadrature Detection
Allows distinction of +/- Frequencies

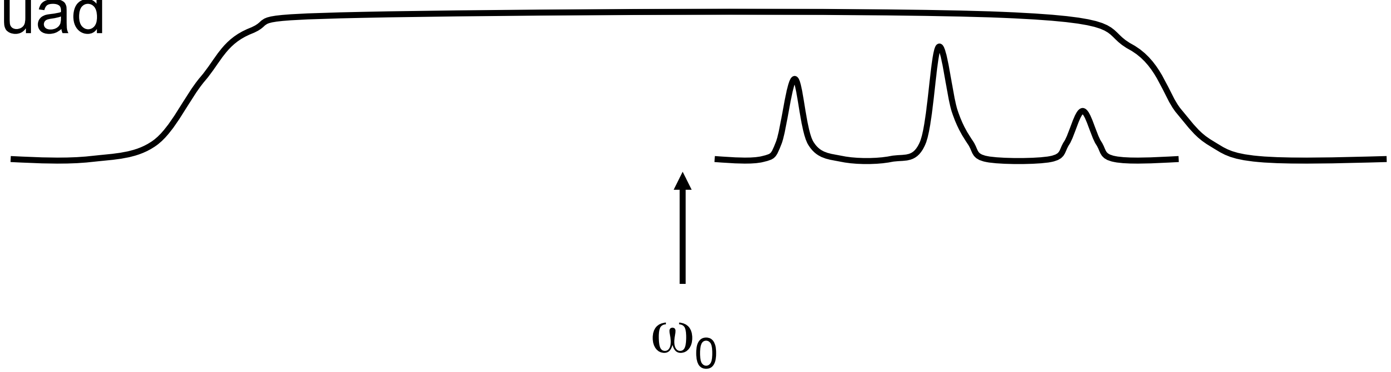




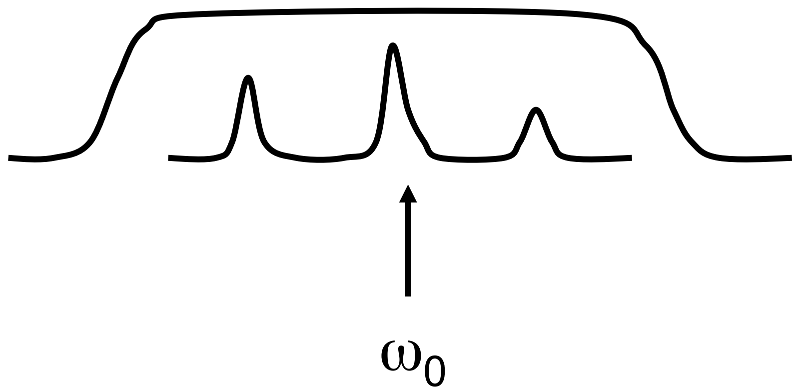
Actually split signal
And use two reference
Frequency phases

Why use Quadrature Detection?
To put ω_{ref} in middle of spectrum.

No Quad



With Quad



Reduced band width of audio filter increases S/N by $1/\sqrt{2}$

Can use reduced transmitter power