NMR Theory
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Magnetic resonance is observed in systems where the magnetic constituents have **both** a **magnetic moment** and an **angular momentum.** Many, but not all, of the stable nuclei of ordinary matter have this property. In "classical physics" terms, magnetic nuclei act like a small spinning bar magnet. For this instrument, we will only be concerned with one nucleus, the nucleus of hydrogen, which is a single proton. The proton can be thought of as a small spinning bar magnet with a magnetic moment μ and an angular momentum $\mathbf{J}$, which are related by the vector equation:

$$\mu = \gamma \mathbf{J} \qquad (1.1)$$

where γ is called the "gyromagnetic ratio." The nuclear angular momentum is quantized in units of h as:

$$\mathbf{J} = \hbar \mathbf{I} \qquad (2.1)$$

where I is the "spin" of the nucleus.
The magnetic energy U of the nucleus in an external magnetic field is

$$U = -\mu \cdot \mathbf{B} \qquad (3.1)$$

If the magnetic field is in the z-direction, then the magnetic energy is

$$U = -\mu_z B_o = -\gamma \hbar I_z B_o \qquad (4.1)$$

Quantum mechanics requires that the allowed values of I_z, m_I be quantized as

$$m_I = I, \ I-1, \ I-2, \ I-3, \ \cdots\cdots\cdots \ -I. \qquad (5.1)$$

For the proton, with spin one half (I = 1/2), the allowed values of I_z are simply

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$$m_I = \pm\, 1/2 \qquad (6.1)$$

which means there are only two magnetic energy states for a proton residing in a constant magnetic field B_0. These are shown in figure 1.1. The energy separation between the two states ΔU can be written in terms of an angular frequency or as

$$\Delta U = \hbar\omega_0 = \gamma\hbar B_0 \quad or \quad \boxed{\omega_0 = \gamma B_0} \qquad (7.1)$$

Fig. 1.1
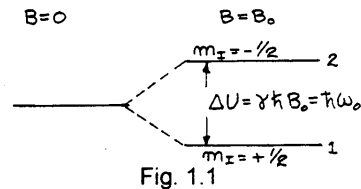
This is the fundamental resonance condition. . For the proton

$$\gamma_{proton} = 2.675 \times 10^4 ; rad/\,sec\text{--}gauss* \qquad (8.1)$$

so that the resonant frequency is related to the constant magnetic field for the proton by

$$\boxed{f_0\ (\text{MHz}) = 4.258\ B_0\,(\text{killogauss}) \qquad (9.1)}$$

a number worth remembering.

If a one milliliter (ml) sample of water (containing about 7×10^{19} protons) is placed in a magnetic field in the z-direction, a nuclear magnetization in the z-direction eventually becomes established. This nuclear magnetization occurs because of unequal population of the two possible quantum states . If N_1 and N_2 are the number of spins per unit volume in the respective states, then the population ratio (N_2 / N_1), in thermal equilibrium, is given by the Boltzmann factor as

$$\left[\frac{N_2}{N_1}\right] = e^{-\frac{\Delta U}{kT}} = e^{-\frac{\hbar\omega_0}{kT}} \qquad (10.1)$$

and the magnetization is

$$M_z = (\,N_1 - N_2\,)\mu \qquad (11.1)$$

The thermal equilibrium magnetization per unit volume for N magnetic moments is

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*Gauss has been the traditional unit to measure magnetic fields in NMR but the tesla is the proper SI unit, where 1 tesla = 10^4 gauss.

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$$M_0 = N\mu\tanh(\frac{\mu B}{kT}) \approx N\frac{\mu^2 B}{kT} \qquad (12.1)$$

where $N = N_1 + N_2$

This magnetization does *not* appear instantaneously when the sample is placed in the magnetic field. It takes a finite time for the magnetization to build up to its equilibrium value along the direction of the magnetic field (which we define as the z-axis). For most systems, the z-component of the magnetization is observed to grow exponentially as depicted in Figure 2.1. The differential equation that describes such a process assumes the rate of approach to equilibrium is proportional to the separation from equilibrium :

$$\frac{dM_z}{dt} = \frac{M_0 - M_z}{T_1} \qquad (13.1)$$

Fig. 2.1
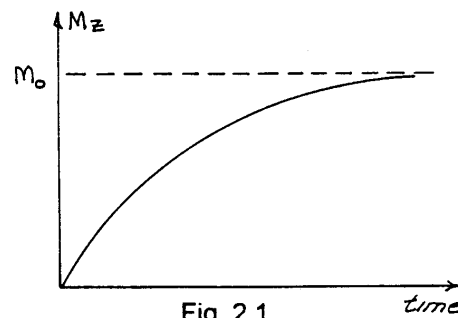
where T_1 is called the spin-lattice relaxation time. If the unmagnetized sample is placed in a magnetic field, so that at $t = 0$, $M_z = 0$, then direct integration of equation 13.1, with these initial conditions, gives

$$M_z(t) = M_0(1 - e^{-\frac{t}{T_1}}) \qquad (14.1)$$

The rate at which the magnetization approaches its thermal equilibrium value is characteristic of the particular sample. Typical values range from microseconds to seconds. What makes one material take 10 μs to reach equilibrium while another material (also with protons as the nuclear magnets) takes 3 seconds? Obviously, some processes in the material make the protons "relax" towards equilibrium at different rates. The study of these processes is one of the major topics in magnetic resonance.

Although we will not attempt to discuss these processes in detail, a few ideas are worth noting. In thermal equilibrium more protons are in the lower energy state than the upper. When the unmagnetized sample was first put in the magnet, the protons occupied the two states equally that is ($N_1 = N_2$). During the magnetization process energy must flow *from* the nuclei *to* the surroundings, since the magnetic energy from the spins is reduced. The surroundings which absorb this energy is referred to as "the lattice", even for liquids or gases. Thus, the name "spin-lattice" relaxation time for the characteristic time of this energy flow.

However, there is more than energy flow that occurs in this process of magnetization. Each proton has angular momentum (as well as a magnetic moment) and the angular momentum must also be transferred from the spins to the lattice during magnetization. In quantum mechanical terms, the lattice must have angular momentum states available when a spin goes from $m_I = -1/2$ to $m_I = +1/2$. In classical physics terms, the spins must experience a *torque* capable of changing their angular momentum. The existence of such states is usually the critical determining factor in explaining the enormous differences in T_1 for various materials. Pulsed NMR is ideally suited for making precise measurements of this important relaxation time. The pulse technique gives a direct unambiguous measurement, where as cw spectrometers use a difficult, indirect, and imprecise technique to measure the same quantity.

What about magnetization in the x-y plane? In thermal equilibrium the only net magnetization of the sample is M_z, the magnetization along the external constant magnetic field. This can be understood from a simple classical model of the system. Think of placing a collection of tiny current loops in a magnetic field. The torque τ on the loop is $\mu \times B$ and that torque causes the angular momentum of the loop to change, as given by:

$$\tau = \frac{dJ}{dt} \quad or \quad \mu \times B = \frac{dJ}{dt} \qquad (15.1)$$

which for our protons becomes

$$\mu \times B = \frac{1}{\gamma} \frac{d\mu}{dt} \qquad (16.1)$$

Equation 16.1 is the classical equation describing the time variation of the magnetic moment of the proton in a magnetic field. It can be shown from equation 16.1 that the magnetic moment will execute precessional motion, depicted in Figure 3.1. The precessional frequency $\omega_0 = \gamma B_0$ is just the resonant frequency in equation 7.1.
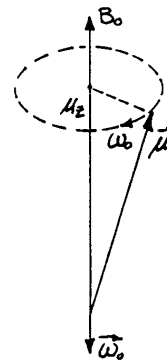

Fig.3.1

If we add up all the magnetization for the 10^{20} protons in our sample in thermal equilibrium, the μ_z components sum to M_z, but the x and y components of the individual magnetic moments add to zero. For the x-components of every proton to add up to some M_x, there must be a definite phase relationship among all the precessing spins. For example, we might start the precessional motion with the x-component of the spins lined up along the x-axis. But that is not the case for a

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sample simply placed in a magnet. In thermal equilibrium the spin components in the x-y plane are randomly positioned. Thus, in thermal equilibrium there is no transverse (x and y) component of the net magnetization of the sample. However, as we shall soon see, there is a way to *create* such a transverse magnetization using radio frequency pulsed magnetic fields. The idea is to rotate the thermal equilibrium magnetization M_z into the x-y plane and thus create a temporary M_x and M_y. Let's see how this is done.

Equation 16.1 can be generalized to describe the classical motion of the net magnetization of the entire sample. It is

$$\frac{d\mathbf{M}}{dt} = \gamma \mathbf{M} \times \mathbf{B} \qquad (17.1)$$

where **B** is any magnetic field, including time dependent rotating fields. Suppose we apply not only a constant magnetic field $B_0\hat{k}$, but a rotating (circularly polarized) magnetic field of frequency ω in the X-y plane so the **total** field is written as *

$$\mathbf{B}(t) = B_1\cos\omega t\,\hat{i} + B_1\sin\omega t\,\hat{j} + B_0\hat{k} \qquad (18.1)$$

The analysis of the magnetization in this complicated time dependent magnetic field can best be carried out in a noninertial rotating coordinate system. The coordinate system of choice is rotating at the same angular frequency as the rotating magnetic field with its axis in the direction of the static magnetic field. In this rotating coordinate system the rotating magnetic field appears to be stationary and aligned along the x*-axis (Fig. 4.1). However, from the point of view of the rotating coordinate system, B_0 and B_1 are not the only magnetic field. An **effective field** along the z*- direction, of magnitude - $\frac{\omega}{\gamma}\hat{k}^*$ must also be included. Let's justify this new effective magnetic field with the following physical argument.

Equations 16.1 and 17.1 predict the precessional motion of a magnetization in a constant magnetic field $B_0\hat{k}$. Suppose one observes this precessional motion from a rotating coordinate system which rotates at the precessional frequency. In this frame of reference the magnetization appears stationary, in some fixed position. The only way a magnetization can remain fixed in space is if there is no torque on it. If the magnetic field is zero in the reference frame, then the torque on **M** is always zero no matter what direction **M** is oriented. The magnetic field is zero (in the rotating frame) if we add the effective field $-\frac{\omega}{\gamma}\hat{k}^*$ which is equal to $B_0\hat{k}^*$.

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* What is actually applied is an oscillating field $2B_1\cos\omega t\,\hat{i}$ but that can be decomposed into two counter rotating fields $B_1(\cos\omega t\,\hat{i} + \sin\omega t\,\hat{j}) + B_1(\cos\omega t\,\hat{i} - \sin\omega t\,\hat{j})$. The counter rotating field can be shown to have no practical affects on the spin system and can be ignored in this analysis.

Transforming the magnetic field expression in equation (18.1) into such a rotating coordinate system, the total magnet field in the rotating frame $\mathbf{B}^*$ is

$$\mathbf{B}^*_{eff} = B_1 \hat{i}* + (B_0 - \frac{\omega}{\gamma})\hat{k}* \qquad (19.1)$$

shown in Figure 4.1. The classical equation of motion of the magnetization as observed in the rotating frame is then

$$\frac{d\mathbf{M}}{dt} = \gamma \, \mathbf{M} \times \mathbf{B}^*_{eff} \qquad (20.1)$$

which shows that $\mathbf{M}$ will precess about $\mathbf{B}^*_{eff}$ in the rotating frame.
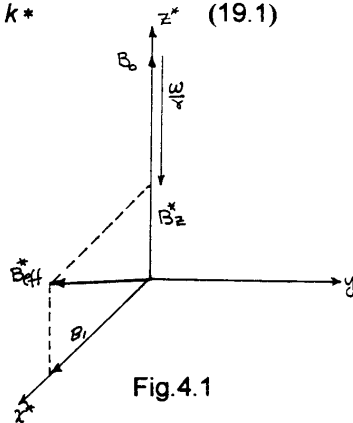

Fig.4.1

Suppose now, we create a rotating magnetic field at a frequency ω_0 as such that

$$\frac{\omega}{\gamma} = B_0 \qquad or \qquad \omega = \gamma B_0 = \omega_0 \qquad (21.1)$$

In that case, $\mathbf{B}_{eff}^* = B_1 \hat{i}*$, a constant magnetic field in the x^*- direction. Then the magnetization M_z begins to precess about this magnetic field at a rate $\Omega = \gamma B_1$ (in the rotating frame). If we **turn off** the B_1 field at the instant the magnetization reaches the x-y plane, we will have created a transient (non-thermal equilibrium) situation where there *is* a net magnetization in the x-y plane. If this rotating field is applied for twice the time the transient magnetization will be $-M_z$ and if it is left on four times as long the magnetization will be back where it started, with M_z along the z^*-axis . These are called:
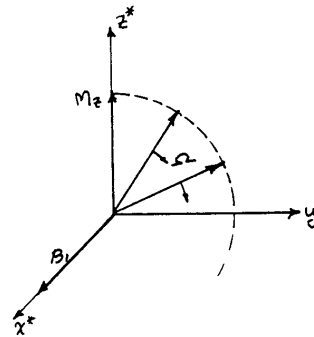

Fig.5.1

$$90° \text{ or } \pi/2 \text{ pulse} \rightarrow M_z \rightarrow M_y$$
$$180° \text{ or } \pi \text{ pulse} \rightarrow M_z \rightarrow -M_z$$
$$360° \text{ or } 2\pi \text{ pulse} \rightarrow M_z \rightarrow M_z$$

In the laboratory (or rest) frame where the experiment is actually carried out, the magnetization not only precesses about B_1 but rotates about $\hat{k}$ during the pulse. It is not possible, however, to observe the magnetization **during** the pulse. Pulsed NMR signals are observed AFTER THE TRANSMITTER PULSE IS OVER. But,

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what is there to observe AFTER the transmitter pulse is over? The spectrometer detects the **net magnetization precessing about the constant magnetic field $B_0\hat{k}$ in the x-y plane. Nothing Else!**

Suppose a 90° ($\pi/2$) pulse is imposed on a sample **in thermal equilibrium.** The net equilibrium magnetization will be rotated into the x-y plane where it will precesses about $B_0\hat{k}$. But the x-y magnetization will not last forever. For most systems, this magnetization decays exponentially as shown in Figure 6.1. The differential equations which describe the decay in the rotating coordinate system are:

$$\frac{dM_{x'}}{dt} = -\frac{M_{x'}}{T_2} \quad \text{and} \quad \frac{dM_{y'}}{dt} = -\frac{M_{y'}}{T_2} \qquad (22.1)$$

whose solutions are

$$M_{x'}(t) = M_0 e^{-\frac{t}{T_2}} \quad \text{and} \quad M_{y'} = M_0 e^{-\frac{t}{T_2}} \qquad (23.1)$$

Fig. 6.1

where the characteristic decay time T_2 is called the Spin-Spin Relaxation Time. One simple way to understand this relaxation process from the classical perspective, is to recall that each proton is itself a magnet and produces a magnetic field at its neighbors. Therefore for a given distribution o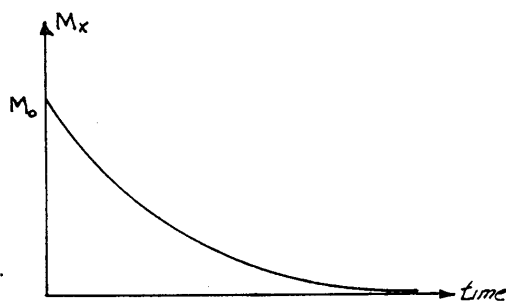f these protons there must also be a distribution of *local* fields at the various proton sites. Thus, the protons precess about $B_0\hat{k}$ with a distribution of frequencies, not a single frequency ω_0. Even if all the protons begin in phase (after the 90° pulse) they will soon get out of phase and the net x-y magnetization will eventually go to zero. A measurement of T_2, the decay constant of the x-y magnetization, gives information about the distribution of local fields at the nuclear sites.

From this analysis it would appear that the spin-spin relaxation time T_2 can simply be determined by plotting the decay of M_x (or M_y) after a 90° pulse. This signal is called the *free precession or free induction decay (* FID) . If the magnet's field were perfectly uniform over the entire sample volume, then the time constant associated with the free induction decay would be T_2. But in most cases it is the magnet's nonuniformity that is responsible for the observed decay constant of the FID. The PSI-A's magnet, at its "sweet spot," has sufficient uniformity to produce at least a .3 millisecond delay time. Thus, for a sample whose $T_2 < .3$ms the free

induction decay constant is also the T_2 of the sample. But what if T_2 is actually .4msec or longer? The observed decay will still be about .3ms. Here is where the genius of Erwin Hahn's discovery of the spin echo plays its crucial role.

Before the invention of pulsed NMR, the only way to measure the real T_2 was to improve the magnets homogeneity and make the sample smaller. But, PNMR changed this. Suppose we use a two pulse sequence, the first one 90° and the second one, turned on a time τ later, a 180° pulse. What happens? Figure 7.1 shows pulse sequence and Figure 8.1 shows the progression of the magnetization in the rotating frame.
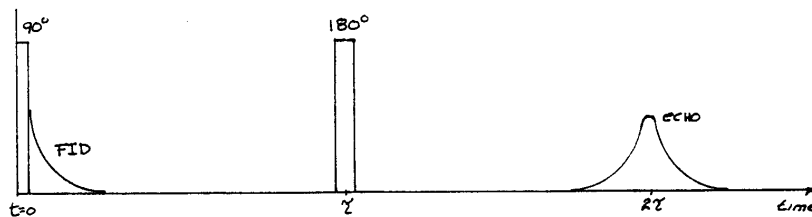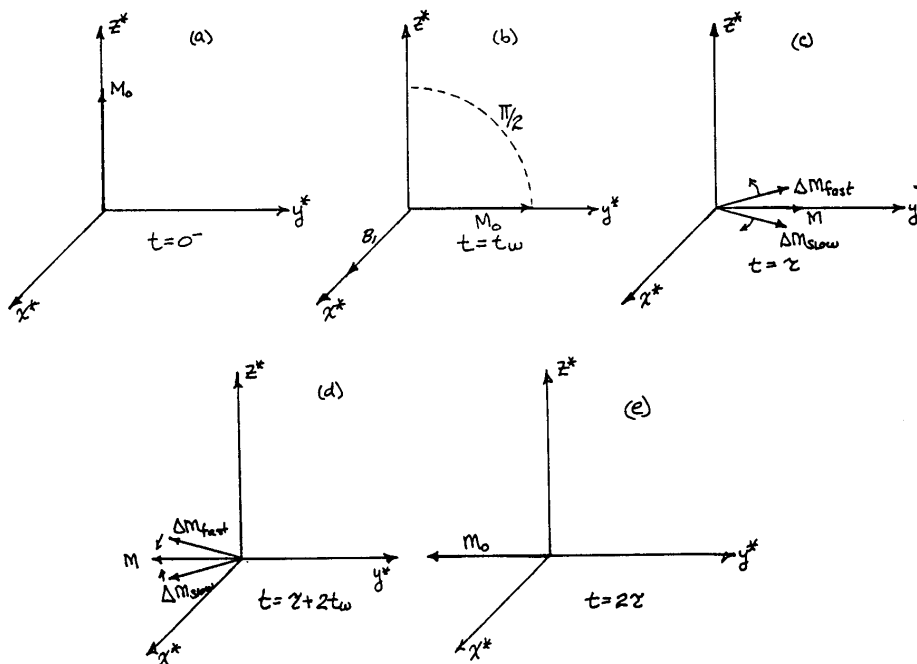

Fig 7.1

Fig. 8.1 : a) Thermal equilibrium magnetization along the z axis before the rf pulse. b) M_o rotated to the y-axis after the 90° pulse. c) The magnetization in the x-y plane is decreasing because some spins Δm_{fast} are in a higher field , and some Δm_{slow} in a lower field static field . d) spins are rotated 180° (flip the entire x-y plane like a pancake on the griddle) by the pulsed rf magnetic field. e) The rephasing the three magnetization "bundles" to form an echo at $t = 2\tau$.

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Study these diagrams carefully. The 180° pulse allows the x-y magnetization to rephase to the value it would have had with a perfect magnet. This is analogous to an egalitarian foot race for the kindergarten class; the race that makes everyone in the class a winner. Suppose you made the following rules. Each kid would run in a straight line as fast as he or she could and when the teacher blows the whistle, every child would turn around and run back to the finish line, again as fast as he or she can run. The faster runners go farther, but must return a greater distance and the slower ones go less distance, but all reach the finish line at the same time. The 180° pulse is like that whistle. The spins in the larger field get out of phase by $+\Delta\theta$ in a time τ. After the 180° pulse, they continue to precess faster than M but at 2τ they return to the in-phase condition. The slower precessing spins do just the opposite, but again rephase after a time 2τ..

Yet some loss of $M_{x,y}$ magnetization has occurred and the maximum height of the echo is not the same as the maximum height of the FID. This loss of transverse magnetization occurs because of stochastic fluctuation in the local fields at the nuclear sites which is not rephasable by the 180° pulse. These are the real T_2 processes that we are interested in measuring. A series of 90°-τ-180° pulse experiments, varying τ, and plotting the echo height as a function of time between the FID and the echo, will give us the "real" T_2

The transverse magnetization as measured by the maximum echo height is written as:

$$M_{x,y}(2\tau) = M_0\,e^{-\frac{2\tau}{T_2}} \qquad (24.1)$$

That's enough theory for now. **Let's summarize:**
1. Magnetic resonance is observed in systems whose constituent particles have both a magnetic moment and angular momentum.

2. The resonant frequency of the system depends on the applied magnetic field in accordance with the relationship $\omega_0 = \gamma B_0$ where

$$\gamma_{proton} = 2.675 \times 10^4\ rad/\ sec\text{--}gauss$$
or
$$f_0 = 4.258\ \text{MHz/kilogauss}$$

3. The thermal equilibrium magnetization is parallel to the applied magnetic field, and approaches equilibrium following an exponential rise characterized by the constant T_1 the spin-lattice relaxation time.

4. Classically, the magnetization obeys the differential equation

$$\frac{d\mathbf{M}}{dt} = \gamma(\mathbf{M} \times \mathbf{B})$$

where **B** may be a time dependent field.

5. Pulsed NMR employs a rotating radio frequency magnetic field described by

$$\mathbf{B}(t) = B_1\cos\omega t\,\hat{i} + B_1\sin\omega t\,\hat{j} + B_0\hat{k}$$

6. The easiest way to analyze the motion of the magnetization during and after the rf pulsed magnetic field is to transform into a rotating coordinate system. If the system is rotating at an angular frequency ω along the direction of the magnetic field, a fictitious magnetic field must be added to the real fields such that the total effective magnetic field in the rotating frame is:

$$\mathbf{B}^*_{eff} = H_1\hat{i}^* + (B_0 - \frac{\omega}{k})\hat{k}^*$$

7. On resonance $\omega = \omega_0 = \gamma B_0$ and $\mathbf{B}^*_{eff} = H_1\hat{i}^*$. In the rotating frame during the pulse the spins precess around $\mathbf{B}^*_1$,

8. A 90° pulse is one where the pulse is left on just long enough (t_w) for the equilibrium magnetization M_o to rotate to the x-y plane. That is;

$$\omega_1 t_w = \pi/2 \text{ radians} \quad \text{or} \quad t_w = \frac{\pi}{2\omega_1}$$

But

$$\omega_1 = \gamma B_1 \quad (\text{ since the } B_1 \text{ is the only field in the rotating frame on resonance })$$

So,

$$t_w(90°) = \frac{\pi}{2\gamma B_1} \quad \text{duration of the 90° pulse} \quad (25.1)$$

9. T_2 - the spin-spin relaxation time is the characteristic decay time for the nuclear magnetization in the x-y (or transverse) plane.

10. The spin-echo experiments allow the measurement of T_2 in the presence of a nonuniform static magnetic field. For those cases where the free induction decay time constant, (sometimes written T_2^*) is shorter than the real T_2, the decay of the echo envelope's maximum heights for various times τ, gives the real T_2.

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A complete text with problems, clear explanations, appropriate for advanced undergraduate or graduate level students. Excellent Bibliography. *Any serious student of magnetic resonance should own it.* Everyone should read at least some of it.

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