********** Part 1: Nuclear Magnetism **********

----------Chapter 1: Matter (5) ---------- 18 p---------- ###

1.1 Properties of Nuclei (5). Use nuclear moment as a non-invasive probe, no other way known to get the info it reveals.

1.2 Spin (6).

1.2.1 **Classical and right hand rule** (6)

1.2.2 **Quantum Angular Momentum (6).** The levels of a **quantum rotator**. $L = \sqrt{J(J+1)}\ \hbar$ and E = (rot const B) * J(J+1) and degeneracy at each level = 2J+1 as shown correctly in the figure. I presume this is a 3D rotator, I might go and do this problem at some point -- write Hamiltonian and SE etc. So far he has been just describing a rotating diatomic molecule, but then suddenly he is talking **Zeeman effect** splitting the degeneracy. I think he forgot to point out that this only happens if that molecule has a magnetic moment. Hmmm, not good.

1.2.3 **Spin Angular Momentum** (7). Comment on the intrinsic-ness of spin. **Fermions** and **bosons**. Spin continues at absolute zero. I know spin as a quantum label of course. I know an electron as a spin 1/2 representation of the rotation group, but this of course does not get much mention. Comment that spin is hard to understand because it **does not "make it" to the macro world**, the way mass does. Comment on **Dirac equation** explaining spin to some extent. No one really understands spin, he says.

1.2.4. **Combining angular momentum** (9). I know this as $\mathbf{J_1} \otimes \mathbf{J_2}$ where you are doing a direct product of two SO(3) representations. He lists off the values of J obtained in the sum of irreducible representations. You can of course apply this idea to nuclear spins. A system of two spin-1/2 particles then has S = 0 or S = 1 which form a singlet and triplet.

1.2.5 **The Pauli Principle** (10). Two fermions cannot be in the same state.

1.3 Atomic and Molecular Structure (10).

1.3.1. **The Particles**(10). Mentions **leptons**, **quarks**, force particles like photon and vector bosons and gluons for EM, weak and strongs. Does not mention graviton for Grav. He seems to accept the quark theory as truth, I still don't like that much.

1.3.2. **Neutrons and Protons** (11). Draws the **3-quark model** for a neutron and on next page for a proton. Fine, but now we forget quarks.

1.3.3 **The atomic nucleus** (12). Parameters are: **Z** = **atomic number** = # protons only. **Mass number** is total protons + neutrons. Notation puts mass as left superscript, while Z is encoded in the element name like C. So we have ^{12}C for example. Number of neutrons for given Z can vary, giving **isotopes** of elements. Claim that most atomic nuclei have spin.

Now look at Figure 1.6 which got my attention. The state |proton,neutron> could be I = 0 or I = 1 in terms of **isospin**. In terms of hadronics, I think I=0 would have the lower energy. Therefore, assuming orbital $\ell = 0$, you must have S = 1 for the ground state to get overall antisymmetric. In this book, spin is confusingly (to me) denoted by I, so I does not stand for isospin as it does in particle physics. In any event, this is a rough explanation of **why the ground state of ^{2}H has spin 1 and not spin 0**. Malcolm makes no mention of isospin or t**he "total asymmetry wavefunction rule" for fermions**, he just shows this figure as a fact. And that is the right approach for a book on NMR perhaps.

Table on next page shows the **ground state spin for various atoms used in NMR**, and also gives natural abundances. Most atoms have a non-zero spin for the nuclear ground state, and those are the atoms we can peek at. Of course any atom with an odd nuclear count must have spin.

Page 15 gives a few spin rules, but there is no perfect general rule for determining ground state nuclear spin.

Rule #1: if number of **protons is even** and number of **neutrons is even**, **spin = 0** (as in |pp>)

Rule #2: if both these numbers are odd, then spin > 0 (as we say in the |pn> case)

I think I could add my own Rule #3:

Rule #3: if total number of protons + neutrons = odd, spin > 0.

1.3.4 **Atoms** (15). Comments on orbitals and ℓ value, s and p and stuff. **Fine structure** due to L-S coupling for the electron, then **hyperfine structure** when you couple the nuclear spin.

1.3.5 **Molecules** (16). Example of **O_2 which has *electron* spin = 1 in the ground state**. In NO, $\ell > 0$ interestingly. Usually you have $\ell = 0$. In Gray, you talk about "molecular orbitals" and binding and non-binding and all that stuff, not mentioned here yet. New word for me: **isotop'omers** are molecules of different mass, otherwise the same, due to isotopes in the constituent atoms. Claim is that total mass and of course underlying atomic masses **affect vibrational levels**, which seems pretty reasonable, so chemical rates affected. And **diffusion** rates affected directly by mass so can separate by GC.

As for NMR, isotopomers behave differently just as isotopes due, since the nuclear spin is affected by which iso you have. Comment that ^{12}C has mass of exactly 12 "**daltons**" Da, a biological term. Mass in other worlds is grams/mole or just grams.

1.4 States of Matter (17)

1.4.1 **Gases** (17). Definition is that a gas **will fill any volume** you let it into. Liquid under gravity at least does not do that, and certainly a solid doesn't. Generally NMR is not done on gases because the density and hence the signal are very low, **exception is xenon** used to map out hidden cavities. To do this, you **pump** up the xenon to a high spin state to increase the signal, see note 5.

1.4.2 **Liquids** (18). High density, and **shear force makes it "flow".** Solids don't flow. Relating to NMR, in a liquid small scale motions average out, like rotations. Special class is **liquid crystals** where flow characteristics are not isotropic. Example of LC are elliptical lined up molecules which have some local direction sense called **the director**, picture top page 19.

1.4.3 **Solids** (19). Resist shear force. Glass flows slowly in fact. Metals are subgroup with high electron mobility. Even in a solid, there can be vigorous local motion, such as fullerene rotation or methyl groups. Claim that solids have "broader" NMR spectra, perhaps due to local motions of things being not washed out as in a liquid, I am not clear on this point.

Notes, Reading, Exercises (21). Gives **Sakurai** QM updated I guess in 1994 or so by the same Sakurai who did the 1967 edition, a gap of 27 years from first to second edition, word "advanced" replaced by "modern". I notice on Amazon that **Shankar** has his QM book going, a 1994 Springer second edition. Lots of Amazon reviews here. Shankar was Yale chairman for a while, lots of good web page info, he has remained himself, 1/ego. I should shoot off an email.

---------- **Chapter 2: Magnetism (23)** ---------- **20 p** ------ ###

2.1 The EM field (23). We are talking E and B, H has no role to play here. **1 T = 10,000 Gauss**. Magnets are now **4-20T**. Mention of Maxwell, we won't be needing all that stuff.

2.2 Macroscopic magnetism (23). Notion of **magnetic moment**. You can **induce** a moment or you can use **ready-made** moments. The induced density is $\mathbf{M} = \chi\mathbf{B}$ and all that stuff. Positive χ is **paramagnetic** and tends to be strong, **diamagnetic** has negative χ and tends to be weak. I would go off and review this stuff, but I know it is not going to matter in this book.

Comment: In the electric world you have $\mathbf{P} = \chi\mathbf{E}$ with $\chi = (\varepsilon - 1) > 0$ in both the dia-electric and para-electric cases, meaning whether you induce the dipole moment into atoms, or you line up existing dipoles. So the induced E field lines up with the inducing E field, and you get $D = \varepsilon E > E$. In contrast, in the magnetic world you have $\mathbf{M} = \chi\mathbf{B}$ and χ can have either sign. In the diamagnetic case when you induce moments in "current loops", the B field those induced currents generate opposes the inducing field, this is Lenz' Law. In para and ferro magnetic cases, $\chi > 0$ because you just line things up. In this regard, the para-electric and para-magnetic situations are similar, but the dia-electric and dia-magnetic cases have opposite signs!

2.3 Microscopic magnetism (25). Three sources are electric currents, nuclear magnetic moments, and electron magnetic moments. The particles have $\boldsymbol{\mu} = \gamma\mathbf{S}$ where S is the spin, γ is the **gyromagnetic ratio**. The γ for the electron has been computed to 11 places in QED.

Comment: In NMR we are dealing with pre-made nuclear spins and we are just "lining them up", so we always have the paramagnetic case. We said above that this has $\chi > 0$ always. But since $\boldsymbol{\mu} = \gamma\mathbf{S}$, the things you are lining up have moments $\mathbf{m} = \boldsymbol{\mu}$ which might point either way relative to the spin **S**.

2.4 Spin Precession (27). This is the main act now. Material has random spin vectors. Apply a B field in some direction and they all sit there and **precess on their cones** (absent interactions). [Malcolm does not like the word "cone", does not use it.]

2.5 Larmor Frequency (30). The notion of precession exists very well in classical mechanics and we easily get the Larmor precession frequency $\omega = -\gamma B_0$. Talks about a sign for this frequency. I derived this from the simple torque equation and a classical J vector (see phys quest notes), and later I did a quantum derivation in my "density matrix notes" (with a picture) where you show that what rotates is in fact the operator I_T.

Comment: I did a classical derivation of Larmor motion in phys quest. The quantum derivation I did in the density matrix document, and it is $\mathbf{I}_T$ *operator* that rotates as time progresses. Same result.

2.6 Spin-lattice relaxation and T1 (32). Name came from solid-state work, there is no real lattice in general, it is just the interaction between a spin and its environment. The interaction causes the spin to leak down toward its state of lowest energy, where moments are pointed along the B field. But then thermal energy prevents them from exactly lining up, and you get a **thermal equilibrium** value of magnetization which is of course paramagnetic in nature. Comment that as atoms and molecules violently rotate, this has basically no effect on the nuclear spin. Well, there is a slight tiny interaction and that is why spins line up toward the B field after a while. At room temperature, the amount of lining up is very small because kT ~ 10^{-21} while the flip energy is 10^{-25} J. You can **compute χ for this nuclear paramagnetism**, result on page 34, value is 10^{-9} which is 1000 times smaller than the electron diamagnetism in water. The time it takes for the spins to react to the B field and reach thermal equilibrium is the famous **T_1 value.** Obviously it depends on the material you are doing NMR on, as well as on the nucleus.

2.7. Transverse Magnetism and T2 (36). If you could suddenly jerk all the spins 90 degrees from z to x, you could shift the entire macroscopic M field from the z to the x direction. You then have a transverse magnetization. But this effect fades away as the spins dephase due to different local b fields, and this time is the T_2 time. This is not really a spin-spin effect, it is spin-environment, though there is also a small spin-spin interaction. [We shall see later more detail about doing this jerk.]

2.8 The NMR signal (39). You could install a little coil to sense the transverse magnetization and you would see a little signal like that drawn page 39 which decays over T_2. This is strangely called **FID**, the **"free induction decay"**. The phrase "NMR signal" is also used, a classic phrase. Means the response.

2.9. Electron magnetism (39). Good to mention this here I think. Why don't you get a huge e-spin-MR effect along with your NMR effect? Answer is partly that in most atoms, S = 0 and L = 0 in the ground state, so for electron J = 0. We have S = 0 due to Pauli pairing in ground state materials. There are exceptions like O_2 which has J = S = 1. For such materials, yes, you can do NMR and it is called **EMR** (also called **ESR** or **EPR**). As with nuclear, it is a **paramagnetic effect**. So, author does not answer the question: in O_2 suppose you do your same NMR experiment, why would you not see T1 and T2 effects from the electrons? Well, here are some interesting numbers:

-928.476 362(37) x 10-26 J T-1	electron
1.410 606 633(58) x 10-26 J T-1	proton
-0.966 236 40(23) x 10-26 J T-1	neutron

So if you work up a little semi-classical theory, I think it would explain why the $\mu_{electron}$ is 1000 times larger than that of the proton or neutron. This is mainly a mass effect, but not obvious to me why at this point. And don't forget that the neutron has a moment, not just the proton. So this explains why the ESR fields would not interfere with NMR, because the mag moments are so hugely different. Author does not make this point very well. [Since γ's hugely different, Larmors different, so resonance far away.]

Closing comment: the B field seen by a nuclear spin is affected by the local environment, and that is how NMR works! Called the **chemical shift**.

---------- **Chapter 3: NMR Spectroscopy (43)** ---------- **28 p** --------- ###

3.1 A simple pulse sequence (43). The point here is how people like to draw these pictures, the RF burst followed by the **"free induction delay"** or **FID**. It is a pulsed approach.

3.2 A simple spectrum (43). Equations for the macroscopic transverse spin rotation I agree with including the T_2 time for decay. Then without derivation, we get a picture of the Fourier spectrum of such a decaying waveform. Oddly, I have to go online to find this particular FT. You would think that some book I have would do classical radiation from a damped harmonic oscillator but I don't see it. No one in my books talks about the **Lorentzian line** shape. You take the FT and do magnitude I think. So OK, if nothing else, the lineshape is empirical with a width related by Heisenberg to the decay time. I agree certainly with (3.2) and (3.3) for the lineshape. The width is typically **milli Hz** so super tiny. Fast decay makes broad peak. [Well, I think typical width might be Hz, not mHz. Here is some data from

http://en.wikipedia.org/wiki/Relaxation_(NMR)

BUT: for liquid TMS, protons have T_2 = 5000 msec, larger than things in following table, so for TMS the linewidths are very tiny, order of 50 milliHz, since $\lambda = 1/(\pi T_2)$.

Common relaxation time constants in human tissues

Following is a table of the approximate values of the two relaxation time constants for nonpathological human tissues, just for simple reference.

At a main field of 1.5 T

Tissue Type	**Approximate T_1 value in ms**	**Approximate T_2 value in ms**
Adipose tissues	**240-250**	**60-80**
Whole blood (deoxygenated)	**1350**	**50**
Whole blood (oxygenated)	**1350**	**200**
Cerebrospinal fluid (similar to pure water)	**2200-2400**	**500-1400**
Gray matter of cerebrum	**920**	**100**
White matter of cerebrum	**780**	**90**
Liver	**490**	**40**
Kidneys	**650**	**60-75**
Muscles	**860-900**	**50**

Following is a table of the approximate values of the two relaxation time constants for chemicals that commonly show up in human brain magnetic resonance spectroscopy (MRS) studies, physiologically or pathologically.

At a main field of 1.5 T

Signals of Chemical Groups	**Relative resonance**	**Approximate T_1**	**Approximate T_2**

	frequency	value (ms)	value (ms)
Creatine (Cr) and Phosphocreatine (PCr) [1]	3.0 ppm	gray matter: 1150-1340, white matter: 1050-1360	gray matter: 198-207, white matter: 194-218
N-Acetyl group (NA), mainly from N-Acetylaspartate (NAA) [2]	2.0 ppm	gray matter: 1170-1370, white matter: 1220-1410	gray matter: 388-426, white matter: 436-519
—CH_3 group of Lactate [3]	1.33 ppm (doublet: 1.27 & 1.39 ppm)	(To be listed)	1040

3.3 Isotopomeric spectra (47). Our first molecule of interest is **TMS** = tetra-methyl-silane. Has four methyl groups connected to a silicon atom. The first problem is figuring out what the major isotopomers *are*, and these are derived from the first table into the second table. The H isotopes are very rare so we ignore them. But ^{29}Si is 5% which is major, and ^{13}C is 1% but there are four places to put a ^{13}C, so 4%. Now look at the spectra on page 48. The left peak is from the protons (which have *positive* γ) in TMS where we tune the B field to make the proton Larmor be 400 MHz *negative*. The ^{29}Si Larmor is way off at + 80 MHz. The signs are different because a proton has a moment aligned with its spin, whereas a Si nucleus has a moment opposed to its spin. This does seem rather odd as I think about it. ^{15}N is the simplest case giving such a negative number. Well, notice that the neutron has a negative moment! That must do it. I have never done "nuclear physics" so I never learned anything about this, just another huge "hole" in what I know, despite a physics phud. Maybe later parts of this book will shed light on this. But at least with neutron having a negative moment relative to its spin vector, I can see how γ can come out negative, especially when there are more neutrons than protons. So of course this is the point of tracking the Larmor sign. And so the total spectrum of figure 3.10 on page 48 includes the proton peak and the ^{13}C peak.

3.4. Relative spectra for positive γ (49). In practice, you only get little windows around a Larmor peak of interest, such as the ^{1}H peak or the ^{29}Si peak. Such windows are shown page 49. Each is referred to as a **channel**. In an NMR machine, you can set a **reference frequency** wherever you like, near a peak of interest, and then you can measure frequencies relative to this reference. On page 50, you see an arrow where ω_{ref} is set, and then that point becomes Ω = 0 in the relative spectrum. And of course Ω has a sign. For normal positive γ nuclei, you draw the Ω in the obvious manner as shown page 51, it increases to the right. A warning comment about the way relative frequency axes are labeled in the literature.

3.5 Relative spectra for negative γ (51). So here, both the ref and the Larmor frequency are positive. We do a similar relative shift as shown top page 52. There should be no problem, but for "historical reasons" the relative spectra for negative γ nuclei are always plotted backwards! So instead of seeing what is on the top of figure 3.15, you will see the flip of it with the Ω axis going off to the left. It is unclear right now why they would do that.

3.6 Inhomogeneous broadening (53). Imagine a **linear gradient** in the B field along the z axis as suggested in the picture bottom page 53. This makes the Larmor be a function of z. Then along each horizontal line through the 2D sample, you have a constant Larmor. Spins along that line in the sample will radiate to a certain point in FID spectrum with amplitude proportional to number of spins on the line. This causes the spectrum to be not a line but a broadened thing like the case shown for the bottle. The amplitude is proportional to how much matter the 2D sample has along each horizontal line, and as a result, your spectrum sort of tells you the shape of your sample! This is of course the basis for MRI. The ring example is also shown but of course in that case the spectrum does not precisely give you the geometric shape. It all makes excellent sense, very good examples.

3.7 Chemical shifts (56). The applied B field is of course modified in atomic localities, as suggested by the mag lines in the page 56 picture. *Most* of this modification is due to "electron motion", and so you are sensing probably the expectation value of some magnetization operator in the valence electron ground state. This is **the chemical shift**, known as **Knight shift** in metals. So the Larmor is going to depend on the local electron density, and this can be either dia or para magnetic in effect. Secondly, the spins of nearby nuclei are going to affect things (we shall see they cause splitting), a weaker effect.

Now our first excellent example here is **ethanol** as shown page 57 (I will be consuming some soon, ethane with one OH). We will be looking at the ^{13}C NMR situation and you see there are two places for a ^{13}C to park. We of course don't worry about both at once since occurrence is so low. So we get about 1% for each single C-13 location.

Ignoring splitting, we find that the two isotopomers have different line locations because the two C-13 locations see different electron wavefunctions -- ie, the two C-13 nucleus locations see different micro B fields. For a given reference frequency, the iso II line (group) appears at positive Ω as shown p 57 bottom and the III appears at negative relative frequency Ω. Of course these signs are totally arbitrary, just depending on where you set the reference frequency [both H-1 and C-13 are positive γ]. In real ethanol, you will have about 1% of each of these isotopomers, so you get two general peaks as shown lower page 58. Still ignoring the splitting, the location of the general peak is the chemical shift. The B field here is a typical 4.7 T and the separation of the H-1 and C-13 FID responses is about 2 KHz, whereas recall the Larmors are 50 MHz or more, so this is a small relative separation.

If you double the B field, you pretty much double the chemical shift which does not surprise me (you double the induced magnetization of the electrons), so you really want to talk about a **dimensionless chemical shift δ.** This is done as shown in (3.6) where you pick maybe the big TMS line as a reference so that TMS itself would be at $\delta = 0$. People add some TMS to their specimen to know where $\delta=0$ is located (I think I recall doing this in Chem 11). The δ will be in the ppm range, our example 2 KHz/50 MHz.

Now recall that we had a $\omega_{\mathbf{ref}}$ that we can dial up on our machine. So you can of course associate a $\delta_{\mathbf{ref}}$ with this as shown in 3.7. If you want to reconstruct the absolute relative frequency shift from the deltas, you do it as in 3.8. The term **"high field" nowadays just means small δ,** more history.

Typical shifts are shown page 62 in a **table**, expressed in δ values. For each NMR-nucleus, like ^{13}C in our last example, this picture shows the typical range of values of chemical shift caused by having each kind of chemical group nearby, such as a methyl CH_3 group. This is of course how we tried to reverse engineer the structure of chemicals we were given in class.

3.8 Multiplet structure (61). The **splitting** is pretty easy to understand, at least on the surface. Look at page 63. If you are working on ^{13}C and you have one H nearby, the H nuclear spin can have two states, aligned and opposed, and it alters the local B field accordingly, and you have a doublet with equal peaks.

If *two* H are nearby (on your same carbon), then they are ++ or -- or two cases +- and -+, so you get the 1:2:1 triplet. And on page 64 you see *three* local H's causes a 1:3:3:1 quartet, and we just have the **binomial coefficients** from simple statistics. The total **area** under all the split peaks is the total signal.

Superimposed on the first level of splitting, you can get **fine structure** as shown in the lower picture on page 64, and of course these are due to spins more than one bond away.

In liquids the actual physics of the spin-spin coupling is called **J coupling** (**indirect dipole-dipole**). If you want to talk about J coupling of a H proton on the same ^{13}C carbon atom as the NMR spin, you call it $^{1}J_{CH}$ where the 1 means one chemical bond away, and the C and H refer to the two coupling spins.

Finally, page 65 shows the ^{1}H *spectrum* of ethanol. The tiny splittings here are proton-proton splittings and are all 3 bonds away as picture shows of ethanol, so these are $^{3}J_{HH}$ **splittings.** The *groups* in this picture show that there are really only two "kinds" of H atoms in ethanol (ignoring the OH one), so that is why there are two line groups, not 5.

Author then explains why the OH H proton does not play a role. **Chemical exchange**, that H is jumping around somehow, and acid base issue. Also, there is no splitting of H by H on the same atom due to their **magnetic equivalence**. Remember, these guys are doing thermal rotation presumably etc etc.

3.9 Heretonuclear decoupling (65). If you want to hide all the spin-spin splittings (two good reasons are given), you can preblast with an RF pulse that I guess randomizes the splitter so it washes out. I vaguely see how this might work, reference is given. The preblast is with the Larmor of the affecting spin, not the affected one.

********** Part 2: The NMR Experiment **********

Digression on IR Spectrometers: In my Chem 11 lab, we used ***infrared*** spectrometers which send IR light through a sample and alternate with an empty sample tube to subtract out lines from the container and solvent. Here you deduce chemical bonds by looking at the **vibrational and rotational absorption**. Instead of plotting against the NMR's δ shift, you see things in cm^{-1} inverse λ. Of course this is IR, not RF, a whole different method.

In the 1960's you would do this by rotating a grating and measure intensity at each frequency, a purely mechanical-optic method. I think this is what I used in my lab. It was only after it became cheap to do a digital Fourier Transform that the FTIR method appeared. Cooley Tukey paper was 1965, but electronics was not cheap probably until 1980 or so, expensive ones appeared in the 1970's. Now the FTIR is the cheapest way to do it, and a unit might cost 3K used and 20K new. Perkin Elmer 1310, 1600 or Spectrum 100 are examples, hard to find prices on the web.

The way an FTIR works is this: First, consider the sum-squared of two electric fields where one has a variable path length relative to the other. The path length difference x is due to a moving mirror. If you square the field to get intensity, and then do a time average so $\langle \cos^2 \rangle = 1/2$, you quickly conclude that

$I(x) = 1 + \cos(kx)$ where x is the path difference, $x = v_{mirror}\, t$

This is a pretty elementary fact, the basis of interference. If you have an IR source with spectrum G(k) [including the effect of your sample in the beam] , then you get

$$I(x) = \int_0^\infty dk\, G(k)\,[\,1 + \cos(kx)\,] = \int_0^\infty dk\, G(k)\,[\,1 + \cos(kx)\,] = I(0) + 1/2 \int_{-\infty}^{\infty} dk\, G(k)\exp(ikx)\,]$$

So you let the mirror do a sweep which varies x over some reasonable range, and this I(x) is seen to be the Fourier Transform of the IR spectrum G(k) [I had to fudge the G(-k) issue, but could get it right if I had to]. So you run your I(x) into an A/D, store samples and sum perhaps over many cycles to remove noise, then do a digital DFT and out comes your G(k) which you then plot on the PC screen. Of course this beam was sent through a sample under test and will have holes in it where there was vibrational or rotational absorption. The point is that it is cheap to have a detector which measures I(x), intensity. No need to disperse the light source in any way. There are theoretical advantages to this method which makes it right. Each mirror scan cycle does the entire spectrum, not just one "line" in the spectrum.

In contrast, an NMR spectrometer has to have a superconducting magnet, so you *know* that is not going to be a low-cost activity. You can see used ones at http://www.labx.com/v2/newad.cfm?catID=18 and they start at about 100K$ and I think you have to provide your own cryogenics! Maybe you just pour in the liquid He and N as needed, from your "supply".

Roberts and Caserio 1964 has an early chapter covering all spectroscopic methods used in chemistry. It's IR example uses a prism to select light, since before the FTIR era. It has a lot on NMR and that is where I studied all the splitting stuff. We never actually *used* an NMR spectrometer, we just learned how to interpret the spectra they made (and I recall being tested on this in 1966 or so).

---------- Chapter 4: The NMR spectrometer (71) ---------- 18 p ------ ###

Signal is weak (nuclear moment is 1/1000th the electron moment + thermal at room temperature randomizes most spins), there is noise, high frequency accuracy is needed. For the first reason, you need about 10^{14} nuclei in your sample.

4.1 The Magnet (71). Field wants to be homogeneous 1 part in 10^9 over 1 cc of sample. You need to keep the magnet at 4 K and that requires both liquid He and an outer liquid N bath as shown in the figure, which bath is 77K. The biggest magnets in 2001 were 21 T which means proton Larmor of 900 MHz. You see machines advertised based on their MHz, by the way. There are lots of so-called shim windings needed to tune the field uniformity. Some are cold, some are not.

4.2 The Transmitter (73). Won't bother with subsections here. You of course have a precise RF synthesizer as shown in the picture. You then have various phase shifters and gate pulse generators to do the tricky pulse sequence preparations used in NMR. We will later see why 0 and $\pi/2$ are called the x and y pulses, but author is saving this for later. The so-called "duplexer" **(Section 4.3)** is a switch shown page 76 which sends in the original RF pulse sequence, then switches while the response comes out. This allows the same coil to be used for excitation and response. This coil is called "the probe" **(Section 4.4)** and it has to make a B field perpendicular to the applied B field. Two capacitors are noted on page 78, one matches impedance, one makes a resonant tank circuit with the coil. Sometimes the sample tube is rotated for averaging purposes. Retune the caps when you change a sample. This whole picture has to be replicated for each "channel" you have.

4.5 The Receiver (80). In the usual L3-style quadrature method, the response is downshifted and heterodyned into the I and Q real signals to get maximal information out. These two response channels I

and Q are separately digitized and there can be some "post" phase shifting in the digital domain, and then we go into the computer for FT analysis. There are two places where phase shift is used, one in the analog sourcing path and a digital one in the digital world, called $\phi_{\mathtt{rec}}$ and $\phi_{\mathtt{dig}}$. This is all shown on page 85 which shows the entire NMR single-channel system. Note that excitation can be with multiple pulses of different phases with precise delay gaps between the pulses, so the pulse generator and delay box do all of that.

Comment: If you supply an RF pulse for a finite pulse time interval, that pulse is going to have a spectrum which has a width which I guess you want to include whatever "spectral lines" you are looking for. So this instrument does not use any kind of dispersion grating or frequency shifting or chirping method (so far). The source of the excitation spectrum is just the fact that the pulse has a natural frequency spread to it that is on the order of $1/\tau$ and of course you can tune this. This is a pretty cheap way to create a spectrum (this point is not made by the author).

Later comment: when we talk about pulse sequences and then the FID response, all is done in the time domain, so "spectrum of the source" never comes up as a topic. The pulse sequence puts the density matrix $\rho(t)$ into some state, and its single-quantum elements then generate the FID, game over. BUT, I think a lot of the discussion assumes "on resonance" for the RF pulse.

---------- Chapter 5: The Fourier Transform in NMR (89) -------- 38 p ------- ###

This chapter surveys several types of NMR "experiments" you might want to perform, discusses the idea of averaging away noise, and then after that talks about doing Fourier Analysis of the results. The notion of having many sample-preparation RF pulses is discussed, but we have no physical motivation in this chapter yet for wanting to do this.

5.1 A Single Pulse Experiment (89). Author makes a lot of "icon drawings" and the one here seems pretty clear, and you see the I and Q waveforms, the Re and Im part of rotating and decaying phasor. An RF pulse lasts a few μS, while the FID might be up to seconds!

5.2 Signal Averaging (90) If you do N repeated "shots", you can improve the S/N ratio by sqrt(N). Graphic on page 93 is good to show how this works. You might do 10,000 shots of 1 second each, so your NMR measurement could take 3 hours!! This is certainly a new feature I was not aware of!

5.3 Multiple Pulse Experiments (93). The situation might look as the top icon p 94 shows -- two pulses at different phases separated by a time interval. For each pulse author specifies with *two* phases, I do not know why this is, but he promises to tell in Chapter 11. The phases always seem to be $\pi/2$ multiples. In an experiment you might cycle over a certain pattern of phases as you do your shots. The motivation so far is totally missing for this kind of sample preparation, but I am sure "we shall see".

5.4 Heteronuclear experiments (95). Up to now, we have assumed we were working with one channel only. But we did see earlier how you might want to shoot some power into a the proton system while you want to look at the C^{13} system because this washes out the splittings to get more signal (Overhauser). So the icon at the top of page 96 shows the top line RF sequence of pulses for "isotope I" while the lower is for "isotope S". Notice how this looks like a musical score for two instruments. We only analyze the FID from the isotope S nuclei, while the other stuff is bystander activation. The top of page 98 shows an experiment where we are applying an amazingly complicated sequence of pulses to at least 4 nuclei at

once, and we are looking only at the FID from the protons on the top line. This is very mysterious right now, but yes, it looks now like an orchestra score. Don't know what GARP means.

5.5 Arrayed Experiments (96). The icon here suggests that we do a set of shots where we adjust the pulse separation t1 between each shot or set of shots. You could then imagine the FID response being FID(t1,t2) where t2 is the conventional time coordinate and t1 is a parameter. You could then do a 2D FT on the result, but not clear right now why that would be meaningful. You could of course extend this to more time parameters and have 3D or more spectroscopy.

5.6 NMR Signal (98). Here we write a single response as |a|*exp[iϕ]* exp[(iΩ-λ)t] to indicate oscillation at the relative frequency Ω and decay with λ and amplitude |a|. The phase just sets the phase at t=0 of the rotating phasor, which could change a cosine to a sine for the real part, and so on. Page 99 shows some examples such a form. Picture top of p 99 is a bit vague for amplitudes I think. He wants ℓ subscript to label individual peaks from different nuclei, all in the same signal. Page 100 shows 4 peaks superposed. Of course we are soon going to do FT to separate out the four spectral lines.

5.7 NMR Spectrum (101).

The FT shown in (5.7) is defined with relative Ω as the frequency variable conjugate to t. We apply this to the complex signal and get a complex spectrum. Author now skips the following math which shows that in effect the FT of a FID is the complex Lorentzian he shows in 5.10. If you set f(t) = u(t) exp(-αt) where u(t) is the Heaviside unit step function, and you do the FT, you get this result: $F(\omega) = 1/(\alpha + i\omega)$ as shown here:

http://www.mas.ecp.fr/Personnel/lilla/classes/image_processing/pdf/FourierTransformPairs.pdf

I have saved this PDF locally, here is the entry of interest:

$u(t)e^{-\alpha t}$	$\frac{1}{\alpha + j\omega}$

meaning 1/[α + iΩ]

Now if we set $\alpha = \lambda - i\,\Omega^0$ as in (5.4), we get the complex **Lorentzian** shown in (5.10),

$$\alpha + i\Omega = \lambda - i\,\Omega^0 + i\Omega = \lambda + i\,(\Omega - \Omega^0) \quad = \text{denominator of 5.10}$$

The complex number a_ℓ in 5.4 just goes along for the ride as a multiplicative factor. Then you get the real and imaginary parts just as he claims (trivial). If you set λ = 0, then $F(\omega) = 1/(-i\omega_0 + i\omega) = -i / (\omega-\omega_0)$ which is a pole at the real frequency ω_0 in the complex result. The absorption is 0, and the dispersion has this pole. On the other hand, if $\omega_0 = 0$, then $F(\omega) = 1/(\lambda+i\omega)$ and this just gives the two parts located at zero frequency $\omega = \omega_o$ with the usual shape as shown top page 103. So, when we do a FT on our FID, we expect to get these shapes for Re and Im parts. The full width at half height is 1/(2λ) and the half height

points are marked by $\omega_o \pm \lambda$ he claims. The pictures top page 103 are what our Re and Im parts say. The Im part changes sign at the resonance, the Re part has a peak.

Now, page 104 bottom shows what we expect for two lines.

In section 5.7.3 we get a layman's explanation of the Fourier transform which leaves me pretty cold. The spectrum has to peak near the line frequency to get a non-zero integral he is saying.

On page 108 he then talks about that complex amplitude again $a = |a|*\exp[i\phi]$. He must points out that this can cause the Re and Im parts to get swapped if $\phi = \pi/2$, say since you are then multiplying both terms by i. You might invert the basic forms as shown. In general, what you get will be given by the equations at the top of page 109, pretty basic.

The last section on page 109 comments that you sometimes get a small "frequency dependent (FD) phase" in addition to the normal phase (due to electronics), and then you need to do a correction. Page 110 top shows in (a) a case of weak FD phase, and its correction to become (b) . The case (c) has a large FD phase which is so large it is inverting the left peak, but again you just correct it. This correction leaves its signature in a slightly "rolling baseline". Right now I have no idea what causes this FD phase or how you do the correction, but he is just getting it on the record.

Now let's look back at our Fourier transform. Hardware deals with real numbers (digital samples of digital hardware), so we write out the FT as follows:

$$FT[\,(s(t)\,] = \left[\int dt\, Re(s(t))\cos(\Omega t) + \int dt\, Im(s(t))\sin(\Omega t)\right]$$

$$+ i\left[\int dt\, Im(s(t))\cos(\Omega t) - \int dt\, Re(s(t))\sin(\Omega t)\right] = A(\Omega) + i\,D(\Omega)$$

As indicated in the picture on page 101, the FT has a real and imaginary part. Our hardware has to do four integrals to get the complete answer. All integrals here are 0 to ∞. We know roughly what the shape of the result is going to be, top page 103. Here we are just showing how the hardware computes them.

NOW, in the above association of Re and Im parts, we have implicitly assumed that a_ℓ is real. Obviously, if a_ℓ we purely positive imaginary, then we get Im = A and Re = -D. This example is shown in the third picture on page 108. So as you vary the phase of a_ℓ , the general appearance of your Re and Im parts is going to change as shown in all these pictures. The first one is the case a = real.

5.8 The 2D Fourier Transforms (110)

Suddenly we postulate the existence of a FID signal as shown top of page 111. We have a single amplitude, but we have two exponentials in two different time variables t1 and t2, each with its own line frequency and damping factor indicated by superscript. Why this should arise, we have no hint at this point. Since the assumed t1,t2 time domain function is separable, we know that the resultant 2D transform is just the *product* of the two complex Lorentzians as shown in (5.22) page 113. If you *then* take the Re and Im parts of this product, you get strange things.

The Re part is shown page 113 in the graph. It is a single peak at the resonant with (x,y) centered at the obvious $\Omega 1$ and $\Omega 2$ location. Close to the peak, the A parts dominate in (5.23) and you get a 2D peak. Away from this peak, the D parts dominate, and you can see it has the dispersion shape there.

The Im part he also writes out, and it is a different mix, AD + DA as shown, not AA - DD. Here close to the center point the A's again dominate and there is a peak, but as you move away, the D's make the peak be a twist peak as shown page 114.

Comment: On page 102 you see the A and D functions. For large ω, A goes as $1/\omega^2$ D as $1/\omega$. This is why D has "longer tails" -- it has a much slower fall off. See plots in my COSY.doc writeup. Levitt does mention this fact, I just forgot about it.

(114) Here we learn about **the States Method**. You have to do two separate experiments using sin and cos amplitude modulation to get a signal of the form (5.25) for cosine. You run these experiments and process the data as shown, eg, in (5.29). Before doing this, author shows the separate sine and cosine spectra on page 117, they are indeed ugly. But when you combine them as shown, you get a pure absorption result as shown on page 118 with clean, well-defined peaks. Everybody does his 2D spectra this way. It is very fancy, a flow chart is shown page 119. This is the first time I have ever heard of such a thing, so I am happy to ignore the details for now, I see the desired result which is simply the product of the two 1D absorption spectra, as shown in the equation at the top of page 118. Remember that the main point of doing NMR is to locate the peaks, so the cleaner they are, the better.

Some alternate names for the States Method are stated on page 119.

Comments on States: Assume the conditions given on page 115. On page 116 are some pictures and both are t_1 on one axis and Ω_2 on the other axis. Each picture has two activities because he is assuming there are two terms in S^{cos} which I call $\ell = 1$ and $\ell = 2$. If you were to write the cosine out as the sum of two expos, then it would be clear that the resulting spectrum (with a = real) will have four peaks, and each peak has the form shown in (5.22). When you multiply out, you get Re = AA-DD and Im = AD+DA as shown on page 113. Each such peak is illustrated p 113 and 114, so if you have four of these peaks going and each one looks the same, you end up with the pictures on page 117. This is all what results from a cosine form. The pictures are really showing Re only: the upper one from the cos term has the form AA-DD just mentioned, and the Im part for this is not plotted. For the sine term, we pick up a 1/2i when converting to expos, so this is going to reverse the Re and Im parts and we will have Re having the ugly form AD+DA (modulo overall sign I have not figured out), and this is what the lower picture p 117 shows.

Here is the States fix. Some equations are needed to see what happens.

$\text{Re } S^{cos} = \Sigma\, a \cos(\,)\ \text{Re } L_2$

$\text{Re } S^{sin} = \Sigma\, a \sin(\,)\ \text{Re } L_2$ // because the a's are real

Therefore, $S^{states} = \text{Re } S^{cos} + i\ \text{Re } S^{sin} = \Sigma\, a \exp(...)\ \text{Re } L_2$

Then do the second Fourier transform on the Ω_1 variable to get

$FT(S^{states}) = \Sigma\, a\ L_1\ \text{Re } L_2$

Then finally we get $\text{Re } \{ FT(S^{states}) \} = \Sigma\, a\ \text{Re } L_1\ \text{Re } L_2 = \Sigma\, a\ A_1\ A_2$ as shown top of page 18, very good, all understood. So in practice, imagine you do lots of "shots" varying both $t_1$and t_2 and you store this all in RAM as $s(t_1, t_2)$. I guess you repeat each shot lots of times to reduce noise. These things are already digitized, you probably did that in real time as the shots ran with A/D's. You do all this first for the cos experiment, then for the sin experiment and collect all the data. Then you do the two FT_2 as shown page 119 and store that back in RAM. Then you run through all this data and create the States

signal shown by doing just what the arrows say. Well, you have buffers for each curved edge box, so you point things accordingly. THEN you do the second FT and the thing that comes out nice is the final Re.

So this is a very nice way to get the clean peaks. You have to "find some experiments" that make the sine and cos terms, however, with all the a being real.

Just for fun, here is what happens if we blindly process the "sin terms" in COSY through our same machinery. In this case, we have $a^{cos} = +i$ and $a^{sin} = -i$ and of course sin $\leftrightarrow$ cos. Then we get, using the fact that Re(iz) = –Im(z),

$$\text{Re } S^{cos} = \text{Re}\{ \Sigma\, i \sin(\,)\, L_2 \} = -\,\text{Im}\,\{ \Sigma \sin(\,)\, L_2 \} = -\ \Sigma \sin(\,)\, \text{Im}\, L_2$$

$$\text{Re } S^{sin} = -\,\text{Re}\{\Sigma\, i \cos(\,)\, L_2 \} = +\,\Sigma \cos(\,)\, \text{Im}\, L_2$$

Therefore, $S^{states} = \text{Re } S^{cos} + i\, \text{Re } S^{sin} = -\ \Sigma \sin(\,)\, \text{Im}\, L_2 + i\, \Sigma \cos(\,)\, \text{Im}\, L_2$

$$= i\ \Sigma\ \{\ \cos(\,) + i \sin(\,)\ \}\ \text{Im}\, L_2 \quad = i\ \Sigma \exp(..)\ \text{Im}\, L_2$$

We then do the second FT on exp(..) which produces L_1 so we then have

$$S^{states} = i\, L_1\, \text{Im}\, L_2 \ \Rightarrow\ \ \text{Re}\{S^{states}\} = -\,\text{Im}\{L_1\, \text{Im}\, L_2\} = -\,\text{Im}\, L_1\ \text{Im}\, L_2 = -\,D_1 D_2$$

Really, each a is multiplied by 1/2 so get - (1/2) D_1D_2. This is what Malcolm shows on page 397 bottom for each of the four peaks of an off-diagonal quartet, but I seem to have an extra minus sign. I need the initial sign difference in order to get the proper exp(..), so I like the relative sign difference. Maybe he has the wrong sign.

In any event, the conclusion for COSY is that you improve the quality of the cross-peaks, and you worsen the quality of the diagonal peaks. Based on the above, with a + sign + D_1D_2 the plots shown on page 398 look exactly right to me. Wonder how I would make these in Maple! DONE, it was trivial, see mws file in this directory. I replicate his picture pretty well.

5.9 3D Fourier Transform(119). The final short section just says you can extend this idea to 3D and further if you want.

Comment: We have now had our whirlwind surface-level introduction. Now I guess Malcolm is going to back off and start again at the beginning, and that means we need to do the spins correctly in QM.

********** Part 3: Nuclear Spin Interactions **********

---------- Chapter 6: Review of Quantum Mechanics (127) ---------- 40p --------- ###

This was a very good if unsupported review of QM with some real math examples provided to boot. No need to take notes, just a little outline: [pages 128-168, 40 pages!]

6.1 Functions -- normalization, basis function, vector representation of a lincom of basis functions. The bra-ket notation is introduced by slight of hand. No mention <x|f> is f(x), just association |f> with f(x).
6.2 Operators -- differential given as example (albeit unbounded and pathological), commutation, matrix, inverse, adjoint, Hermitian, unitary, diagonal, etc etc
6.3 Eigenfunctions and eigenvalues -- bra-ket notation continues. Degenerate eigenvalues. Theorems about the eigenvalues of commuting operators on page 139. If degenerate, may have to shuffle.
6.4 Exponential operators -- since this is a book on spin, we have to get quickly to the angular momentum presentation in QM. Theorems for exponentiated operators.
6.5 Cyclic commutation icon, no use of ε symbol. The "sandwich formula" is presented in terms of a set of cyclically commuting operators, but of course might as well do it for rotation operators. The sandwich just shows the operator which rotates another operator about some chosen axis. Pictures. Sort of similarity transformation in the matrix world, or whatever.
6.6 Spinless QM. Statement of the time dependent Schrodinger equation with its Hamiltonian, but no explanation of H, just an example given for particle in a deep box 1D. Probabilities for observables which are all Hermitian operators.
6.7 Energy Levels , example for particle in box
6.8 Natural units where $\hbar = 1$, rewrite the SE.
6.9 Superposition of states, stationary states just propagate in time with a phase. Drops the phrase "quantum numbers" without a definition, but we know these are the energy level labels in this case.
6.10 Conservation laws. Quantity Q is "conserved" if its operator Q commutes with H. Then H itself is conserved, energy conservation.
6.11 Angular momentum. Writes **L** = **r** x **p** but expresses it as $\boldsymbol{\ell}$ = -i **r** x **D** where D = diff op. No explanation of why this is "angular momentum" or even what AM is. We can verify that $\boldsymbol{\ell}$ so defined has components which cyclically commute, hence they do the sandwich rules for rotating operators. Raising and lowering operators introduced and how they act on the states which he calls | ℓ,m >, referring to these loosely as "spherical harmonics".
6.12 Spin is just the I property like the ℓ thing of the last section, intrinsic spin. Rotation operators in general, trace. States are now called | I, M >.
6.13 Spin-1/2. The two base states are called Zeeman Eigenstates where |α> = up. All operators are shown in their 2x2 matrix form, Pauli guys and so on. Then projection operators in ket-bra notation. I will have to play with these as the need arises.

So, this was a *tour de force* for "what one needs to know to do the QM of spin only". I will have to go back and be more careful and perhaps look at my own angular momentum notes when we start applying this stuff to RF spin sample preparations.