---------- **Chapter 10: Ensemble of Spins-1/2 (273-312)** -------- **39 p** ---------- ###

The goal here is to be able to handle ensembles in thermal equilibrium.

10.1 The Spin Density Operator (273). For a single spin-1/2 this is just defined as in (10.3), same as in Schiff (see below). It is a sum of projection operators. You normalize the sum as shown top of p275. The final result is 10.6 where the left side is the average expectation value of some operator over your ensemble. The answer is you do the trace, and everything is determined by the four complex numbers of the matrix ρ shown in 10.3. See phys quest notes for more on Schiff/Leavitt comparison.

********** **Aside: A Comparison of Schiff and Levitt on the Density Operator** **********

Schiff always seems to have everything. He does the density operator on page 378. He comments on the idea in classical physics of a region of phase space and the idea of how a quantum state might be blurred out into this phase space region and that is somehow the role of the quantum theory density operator.

Equation (42.1) tells you about the expectation value of some variable Ω in state α, but expresses it in an odd form where you project out of each i,j state pair the part belonging to α and you add these i,j contributions up with an implied i,j summation. The right side of (42.1) shows that (42.2) is true, and you have your original expectation value as trace($P_\alpha\Omega$) where $P_\alpha = |\alpha><\alpha|$ is a **projection operator**. We are at this point dispatched back to page 166 of Schiff where projection operators were introduced. Notice that $tr(P_\alpha) = \Sigma_i <i|\alpha><\alpha|i> = <\alpha|\alpha> = 1$.And also $P_\alpha^2 = |\alpha><\alpha|\alpha><\alpha| = |\alpha>1<\alpha| = P_\alpha$. Schiff goes on to write $i\hbar\partial_t P_\alpha = [H,P_\alpha]$ as the equation of motion. So far, this discussion has nothing to do with statistics.

The next step is to assume that you have some kind of *mixture of states* with random phase differences between the states (whatever that means). If, in your mixed state, the probability of being in state α is p_α, then you can define a **density matrix operator** $\rho = \Sigma_\alpha |\alpha>p_\alpha<\alpha| = \Sigma_\alpha p_\alpha P_\alpha$. This is the first time a sum over α has appeared in this section. He says the α states are orthonormal but they don't need to be complete, but I will think of this α as labeling the states in some "mixture of states".

Now consider:

$$tr(\Omega\rho) = \Sigma_i < i \mid \Omega\rho \mid i > = \Sigma_i < i \mid \Omega [\Sigma_\alpha |\alpha>p_\alpha<\alpha]| i > = \Sigma_\alpha\ p_\alpha\ \Sigma_i\ < i \mid \Omega \mid \alpha><\alpha \mid i >$$

$$= \Sigma_\alpha\ p_\alpha \Sigma_i\ <\alpha \mid i >< i \mid \Omega \mid \alpha> = \Sigma_\alpha\ p_\alpha\ <\alpha \mid \Omega \mid \alpha> = <\Omega>$$

So this shows that in a "mixed state" described by ρ, you have $<\Omega> = tr(\Omega\rho)$. Note that this is not the same as expectation in state α, it is in the mix of states that are labeled by index α.

So, we started with the idea of projection operator P_α for each state α, and we ended up with the idea of a density operator ρ describing a mixture of states. And $i\hbar\partial_t\rho = [H,\rho]$. Everything follows over from P_α to ρ.

Now let's review what Leavitt does on page 274. We are restricted here to the spin-1/2 world. In equation (10.3), the state $|\psi>$ is a specific system state characterized by c_α and c_β. But then he says to construct a mixed state that is the average of states 1,2,3....N where the probability of being in any of these states is $p_\alpha = 1/N$. Then top page 275 really says $\rho = \Sigma_\alpha |\alpha>p_\alpha<\alpha|$ and (10.5) is then just a fine

way to say this. We know from Schiff above that $\langle\Omega\rangle = tr(\Omega\rho)$ and hence we get Malcolm's (10.6). This is the average of the expectation value of some operator in your many states. It is the ensemble average.

Now let's think of our ρ operator as a 2x2 matrix. Then $\langle i|\rho|j\rangle = \Sigma_\alpha [\langle i|\alpha\rangle p_\alpha \langle\alpha| j\rangle = \Sigma_\alpha p_\alpha c_i^\alpha c_j^{\alpha\bullet}$

which you would write as $< c_i c_j^\bullet >$ and this is Malcolm's (10.7), just fine. Now he calls the states α and β instead of 1 and 2, so the Schiff α now has a different meaning in Leavitt.

So I am completely happy with Leavitt's and Schiff's density matrix equations, there is no difference as I once thought there was.

Addendum: What is the meaning of the operator $Z_{rs} \equiv |r\rangle\langle s|$? This "off diagonal" operator form does not appear in the density matrix formalism, but we must admit: it is some kind of operator in our Hilbert space. Here I am using rs in place of ij since easier to read. The states $|r\rangle$ might be the eigenstates of some Hamiltonian. To see the meaning of this weird operator, let's examine its matrix elements between two arbitrary states

$$\langle\psi'| Z_{rs} |\psi\rangle = \langle\psi'|r\rangle\langle s|\psi\rangle$$

This matrix element is large to the extent that ψ aligns with s and ψ' aligns with r. Not sure useful.

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10.2 Populations and coherences (275).

10.2.1 Density matrix (275). The "density matrix" shown in (10.7) *is* the density operator in our 2 dimensional Hilbert space of the spin-1/2 system. Both these "density things" describe a statistical ensemble of states.

If we average our density operator over the ensemble, it is called a density matrix. Diagonal elements are populations, off diagonals are coherences.

10.2.2 Box notation (276). Everything is clear here. Notice how you can write the density matrix (an operator) in terms of certain spin matrices defined back on page 165. Two projectors, and the raise/lower guys. The + is upper right corner.

10.2.3 Balls and arrows (276). Just notation for now.

10.2.4 Orders of coherence (277). We first consider the "coherence between two energy eigenstates" r and s. The density matrix is stuffed in there. The idea is that this is general, not spin-1/2 only. If r and s are the same, you are talking a population, not a coherence. If you are doing spin states, then I_z is diagonal and states r and s have M_r and M_s . The difference is defined as the "order p_{rs} of the coherence". We have no idea why this is useful at this point. In the spin 1/2 world, using the only available numbers for M_j you can only produce 0,1 and -1 for your "order of the coherence", but other numbers with larger spins. This does seem rather mysterious at this point.

10.2.5 Relationships (278). Everything is pretty obvious here.

10.2.6 Physical interpretation of the populations (279). If you compute $\langle I_z \rangle$ using the density matrix you get $(\rho_\alpha - \rho_\beta)/2$ so we know this is going to be proportional to the longitudinal magnetization and he shows some pictures of it both ways on page 279. Comments that at room T, very small off random.

10.2.7 Physical interpretation of the coherences (280) . Now compute $\langle I_x \rangle$ and $\langle I_y \rangle$ as shown top page 281, and you see that $\langle I_x \rangle = \mathrm{Re}(\rho_-)$ and $\langle I_y \rangle = \mathrm{Im}(\rho_-)$ so you get the picture shown. So now I can relate the word "coherence" to the idea of transverse spin coherence. I only did this for spin-1/2, not clear exactly what happens with higher spin, I imagine a closely related result, but of course there are now lots of off diagonal elements, not just ρ_- .

Comment: In a statistical ensemble of 2-state systems, the implication of the above discussion is that, from a point of view of computing expectation values of ANY operator for the ensemble, you don't need to know c_α and c_β for every single system which would be 2N complex numbers. Instead, you need only four real numbers which are four components of the density matrix. Two real numbers are the diagonal elements, and the other two real numbers are the real and imaginary part of the one unique off diagonal element. These four numbers completely specify the spin ensemble for purposes just stated. Having more information adds nothing to your calculational abilities. Messiah calls this an incompletely known system.

Problem: Suppose you combine N spins each of spin I. What does the energy level diagram look like with no interactions?

Answer: the levels are spaced from NI down to -NI, integer spacing. This is 2(NI)+1 distinct levels. I could calculate the degeneracy at each level as a function of N and I, but let's not do that here.

10.3 Thermal equilibrium (281). We consider a general spin system with ω_r energy levels, and we first claim that in TE, we expect no transverse mag, so we expect more generally no off-diagonal matrix elements. I will just accept this as proven for spin 1/2 and pretty good guess for higher spins. The TE populations (diagonal elements) are then determined by Boltzmann statistics. Specifically, in 10.15 the denominator summed over our two states is close to 2 (next page), the two numerators are $1 \pm b/2$. Don't confuse Boltzmann b with static field B.

It is noted that at room temperature, we are only about 1 part in 10^5 [but math suggests 1 in 10^4] away from TE even with a huge B field! This makes you wonder how NMR is going to get a strong signal! The "Boltzmann Factor" is here defined as a simple energy ratio 10.16. Since it is so small, we can expand everything in small B and we quickly end up with 10.17 for our density matrix in TE. Rewritten trivially in 10.18. This says that in TE, we have a population difference due to our static B field which is creating our separated energy levels, and we have no off diagonals.

10.4. Move ρ to rotating frame. (284). The general case for this transform of our matrix ρ is given, the diagonals don't change (spin-1/2), the coherences pick up complementary phases equal to the amount of rotation, but the TE matrix is unaffected by this transform since only has diagonal elements. Hence we have 10.22 and line above it.

10.5 Magnetization vector (285). Malcolm messes up a bit here. We already know from top page 281 that 10.23 and 10.24 are correct, but we are unclear about where those normalization factors come from. Here is my answer to that question.

First, we claim that most general hermitian form for scalar hermitian ρ is $\rho = k_1 \mathbf{1} + k_2 \mathbf{M}\bullet\mathbf{I}$ where k_1 and k_2 are some constants. So,

$$\rho = k_1 \mathbf{1} + k_2 \mathbf{M}\bullet\mathbf{I} = [\, k_1 + (k_2/2)M_z,\ (k_2/2)M^-,\ (k_2/2)M^+,\ k_1 - (k_2/2)M_z \,]$$

Now we can compute $\langle I_z \rangle = \mathrm{tr}(\rho I_z) = (k_2/2)M_z$ and doing the others we find $\langle \mathbf{I} \rangle = \mathrm{tr}(\rho \mathbf{I}) = (k_2/2)\mathbf{M}$. Thus, we see that $\mathbf{M} \sim \langle \mathbf{I} \rangle$ so it is appropriate to speak of **M** as the "magnetization vector" up to a proportionality constant. Now, in TE we know that ρ has the form 10.17, so this tells us that $M_x = M_y = 0$ which is an expected result for TE. The diagonal elements tell us that

$$k_1 + (k_2/2)M_z = 1/2 + b/4$$
$$k_1 - (k_2/2)M_z = 1/2 - b/4$$

Adding we find that $k_1 = 1/2$, and subtracting we find that $k_2 M_z = b/2$. If we want **M** to be a *unit vector*, then in this case $M_z = 1$ so we have $k_2 = b/2$. Thus it must be that, for an arbitrary direction of the **M** vector, we have

$$\rho = (1/2)\,\mathbf{1} + (b/2)\,\mathbf{M}\bullet\mathbf{I} = [\, 1/2 + (b/4)M_z,\ (b/4)M^-,\ (b/4)M^+,\ 1/2 - (b/4)M_z \,]$$

as claimed in the first line of 10.26. Also, $\langle \mathbf{I} \rangle = \mathrm{tr}(\rho \mathbf{I}) = (b/4)\mathbf{M}$. All other results on this page trivially then follow. These things are true in a temperature regime where $b \ll 1$ which includes anything near room temperature.

The idea that $M_x = M_y = 0$ is where we have to assume that the systems in our ensemble have "random phase" relative to each other. This would be expected in thermal equilibrium.

10.6 Strong RF pulse (286). Recall from page 268 (graphs, notes above) that we need (Ω_0/ω_{nut}) to be small if we want to be very close to resonance to use the "at resonance approximation". This means we want ω_{nut} to be large. But $\omega_{nut} = |\, 1/2\ \gamma\ B_{RF}\ |$ so this means we want B_{RF} to be large if we want to assume we are "at resonance", hence the title of this section "strong RF pulse". Recall that ϕ_p is the assumed phase of our RF pulse B field at t=0 when the square shaped pulse starts. We know from earlier work that the state propagator for such an RF field of duration τ_p is $R_{\phi_p}(\beta_p = \omega_{nut}\tau_p)$ as shown mid page 287. It is a rotation of the **M** vector (~ the $\langle \mathbf{I} \rangle$ vector) about an axis in the x,y plane as shown on page 264. This same rotation then is what transforms the density matrix ρ, as shown in 10.27. The pulse here would be called a $(\beta_p)_{\phi_p}$ pulse. It is always assumed that our RF B field is "along the lab x axis" and this has nothing to do whether we have an x-pulse or a y-pulse in the sense of the angle $\phi_p = 0$ or $-\pi/2$.

So, we now know the effect of an arbitrary at-resonance square pulse on our spin-1/2 ensemble. We know exactly how this pulse changes the ρ matrix, and since the density matrix is a complete practical description of our spin system, we know everything there is to know!

What happens if there is no RF pulse? If we try to take the $B_{RF} \rightarrow 0$ limit of the above, we get $\beta \rightarrow 0$ and this says there is no transformation of operator ρ. But this means $\omega_{nut} \rightarrow 0$ so we are not at resonance unless $\Omega_0 = 0$ exactly. So for no RF pulse, it is better to assume a small non-zero Ω_0 . We solved this problem on page 256 see (9.19) which says we get an $R_z\ (\Omega_0 \tau)$ as our propagator. We come back to this subject below on page 293. Our limit gives the right answer for $\Omega_0 = 0$ which is no change, and the result $R_z\ (\Omega_0 \tau)$ is correct for any reasonable Ω_0 between pulses.

So what remains is to look at specific pulse cases and see what happens!

10.6.1 Excitation of coherence (288). We start with our $(\pi/2)_x$ pulse and find that $\rho = (1/2) + (\beta/2)I_z$ becomes $\rho = (1/2) - (\beta/2)I_y$. I did this calculation in full detail, but the shortcut is the geometric picture where $R_x(\pi/2)$ takes spin vector **M** from the z axis to the -y axis, just the way it took our α state (+z) to the -y state in the previous chapter. That is to say, we start with M = (0,0,1) in ρ, and we end up with M = (0,-1,0) in ρ, where $\rho = (1/2)\ \mathbf{1} + (\beta/2)\ \mathbf{M \bullet I}$. As we suspect, after this pulse, we have killed off our population difference and created some off-diagonal terms as shown top page 289. The presence of off diagonal terms means there is now some kind of transverse polarization. [see notes in "confusion about rotation" for how this intuition works.]

Comment: this requires some pondering. We start with an incompletely known TE system which has a population difference (albeit small) due to our static B field. Let's look at a few sample systems. Suppose we had 60% up and 40% down (even though way out of our TE range) and nothing else. All these are rotated to the y axis, and we end up with 60% in -y and 40% in +y. We end up with zero population difference up and down, as predicted. Suppose we had 60% +y and 40% -y? This would result in a net up-down population difference, but this violates the TE rules which say we could only have a 50/50 mix in this case. If we had such a 50/50 y mix, it would rotate into a 50/50 z mix and cause no population difference. So in a crude sense, if you think separately of the three axis cases, you predict the correct result. Basically this pulse rotates the M vector as just stated above and leaves it with nothing in the z direction. The upshot is that a TE ensemble pretty much acts the same way a single +z aligned spin does to the $(\pi/2)_x$ pulse. For a single spin pointing up we have $\langle \mathbf{I} \rangle = (1/2)\hat{\mathbf{z}}$ but in our TE ensemble, on average each spin has $\langle \mathbf{I} \rangle = \mathrm{tr}(\rho \mathbf{I}) = (1/2)\ (\beta/2)\hat{\mathbf{z}}$ so the TE dilutes the effect of the average spin by $(\beta/2) \sim 10^{-5}$. The point is that this TE dilution effect does not change the fundamental effect of a $(\pi/2)_x$ pulse, it's just that the magnetization vector is really $(\beta/2)\ \mathbf{M}$, and the net actual magnetization would be something like $\mu = n(\beta/2)\ \mathbf{M}\ \hbar$ units per cc, where n is the number of spins per cc. Although β is small, n is large, so we are going to see something.

So the density matrix allows us to completely characterize a "beam" of spins (to tie in with other readings) which has an unpolarized component. In our example above, the magnitude of the polarization vector would be very small, only $(\beta/2)$, and our beam is mostly unpolarized due to TE, thermal equilibrium. Beams of light are similar, unless prepared in a special manner.

10.6.2 Population inversion (289). Now we try a $(\pi)_x$ pulse. As expected, it takes $\rho = (1/2) + (\beta/2)I_z$ to $\rho = (1/2) - (\beta/2)I_z$ and this resulting ρ matrix is diagonal and shows in inversion! It swaps the two populations without causing and transverse polarization.

10.6.3. Cycle of states (290). The little cycle shown bottom page 290 makes complete sense, as do the other two pictures. He avoids using the word "polarization" so far. Claim that in the real world, you might do 4 or 5 such complete cycles before relaxation losses set in.

10.6.4. Stimulated absorption and emission (291). This is what is happening here! Your first π_x pulse which causes an inversion is stimulated absorption, the second one does stimulated emission . Remember that we are doing a semi-quantum calculation here: the spin system is treated quantum, but the RF field is treated as a classical field. We could redo all this with the EM field quantized, and see photons created and destroyed. Our states would be spins + photons. If we did it this way, the spontaneous emission would be more obvious. I think it is not going to appear in this semi-classical (yet viable) approach.

10.7 Free precession without relaxation (292). We already looked into this above, end of my 10.6 notes. The propagator is $R_z(\Omega^0\tau)$ if we just sit for time τ. The result is that the populations don't change but the coherences do, they add phase. This is just the spins rotating around on their little cones that Malcolm does not like. The M vector rotates on the surface of a cone, it really does. This is exactly what equations 10.31 say. His picture on page 294 however is drawn as if $M_z = 0$. This would be the right picture if you first applied a $(\pi/2)_x$ pulse which removes the M_z component. At the start of the "silence period" you have M along the -y axis, and then it just rotates in the x,y plane from then on. The pictures on page 295 are showing exactly this happening.

Equation Derivations for this section (added 1.24.08). They were not red-checked by the way, so let's do them now.

We know in general that a scalar operator transforms over time as $\rho' = U\rho U^{-1}$ where $U = \exp(-iHt)$ where H is the Hamiltonian. The reason for this is the SE says $\partial_t\psi = -iH\psi$ which tells us that we have $|\psi(t)> = \exp(-iHt)|\psi(0)> = U|\psi(0)>$. According to our rule that translating time for both experiment and observer, we know that $<\phi|Q|\psi> = <\phi'|Q'\psi'>$ for any operator Q whatsoever, scalar or not. In the case of $Q = \rho$, this then tells us that $\rho'(t) = U\rho(0)U^{-1}$ with $U= \exp(-iHt)$. For a spin-1/2, we have $H = +\Omega^0 I_z$ as in (9.19) on page 256. So we have $U = \exp(-it\Omega^0 I_z) = R_z(+t\Omega^0)$ agreeing with (10.28), so that equation now gets a red check.

Now, suppose we did a "matrix expansion" for $\rho(0)$ [I am using future knowledge here]. We know that the matrix term in this expansion representing such a diagonal element is either 1 or I_z. For example, we know that I_x would cause off-diagonal elements. So, a term that multiplies 1 or I_z will be unaffected by our $R_z(+t\Omega^0)$ and so just stays exactly the same. So red check goes on (10.29). In a 2-spin secular world of AX systems, our U will still be $R_z(..)$ in either I_1 or I_2 and the population terms in ρ will still involve things like I_{1z} or 1 or maybe $I_{1z}I_{2z}$. None of such terms are affected by any R_z and so more generally, populations "stay put" during free propagation. Notice that this theory does not know about spontaneous emission which for NMR is very slow it is said so OK to ignore it.

Clarify one more time. The diagonal terms are those that have matrix elements of the form $<\gamma \mid \rho \mid \gamma>$ and you cannot have any I_x or I_y type terms in ρ for such a term. Therefore, terms are 1 and I_z like. So we don't bother any more thinking about the matrix element, we just thing of the matrix terms.

Equation (10.30) is not quite so obvious, the sign in particular is of interest. We understand now that a term like ρ_+ or $\rho_{+\alpha}$ (both single quantum terms, the second from AX world) is identified with a matrix term in ρ of the form I^+ or $I_1{}^+I_{2z}$ perhaps. The idea is that we will raise the state on the right, and have a

non-zero matrix element, so we must have had $\langle\alpha| I^{+} |\beta\rangle$ to have a non-zero matrix element of ρ. Now the whole thing is quickly explained by the following sandwich formula which does not appear anywhere in Levitt as far as I know:

$$\exp(-i\theta J_z)\ J_{\pm}\ \exp(+i\theta J_z) = \exp(\mp i\theta)\ J_{\pm}$$

We can apply this with $J \rightarrow I$ and $\theta = +t\Omega^0$. We then have U on the left side and we find

$$UI_{\pm}U^{-1} = \exp(\mp it\Omega^0)\ I_{\pm} \qquad\qquad U = \exp(-it\Omega^0 I_z)$$

This then tells us that the sign of the propagation phase is *opposite* the sign of the single-quantum coherence matrix element of ρ which you are looking at. In particular, a ρ_- has the positive phase as shown in 10.30, so another red check please! Malcolm just quotes these results with no comments, no derivations, so we are happy campers now.

BUT: our rule just stated assumes that Ω^0 is defined by $H = +\Omega^0 I_z$. We know this is going to be something like $H = -\mu \bullet B = -\gamma B^0 I_z$ so we identify $\Omega^0 = -\gamma B^0$. For protons $\gamma > 0$, so $\Omega^0 < 0$. Therefore, we can restate our little rule above like so:

Rule: We associate a + coherence with I_+ . We think of α as along the spin or the lower energy state, and this state is reached by doing I_+ on β. So in terms of I_z, we say that α is the upper state, but in terms of energy it is the lower state. In free propagation, we know that a + coherence has phase $-\ it\Omega_0$. For protons, however, we know that $\Omega^0 < 0$, so we can say the phase is really + it $|\ \Omega_0|$. So in this sense, we associate a + coherence with + in the phase with a plus number in the phase as well, but this only applies if $\gamma>0$ which it is for protons.

10.8 Operator transformations (295). // see "confusion about rotation" notes elsewhere.

First, Some Phil Math. I got bogged down here, so consider these facts:

$$R_x(\pi/2)\ I_x\ R_x(-\pi/2) = I_x$$
$$R_x(\pi/2)\ I_y\ R_x(-\pi/2) = I_z$$
$$R_x(\pi/2)\ I_z\ R_x(-\pi/2) = -I_y$$

where the R's are 2x2 spinor matrices. We can represent all three equations as follows:

$R_x(\pi/2)\ \mathbf{I}\ R_x(-\pi/2) = \mathsf{A}\ \mathbf{I}$ where $\mathsf{A} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix}$. Here is a proof that this is correct:

$$\mathsf{A}\ \mathbf{I} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix} \begin{pmatrix} I_x \\ I_y \\ I_z \end{pmatrix} = \begin{pmatrix} I_x \\ I_z \\ -I_y \end{pmatrix}$$

Now claim that in fact $\mathsf{A} = \mathsf{R}_x(-\pi/2)$. To show this is correct, we will show that $\mathsf{A}\,\hat{\mathbf{z}} = +\hat{\mathbf{y}}$:

$$\mathsf{A}\,\hat{\mathbf{z}} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix}\begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} = \hat{\mathbf{y}}.$$

Therefore we have shown that

$$\mathsf{R}_{\mathbf{x}}(\pi/2)\ \mathbf{I}\ \mathsf{R}_{\mathbf{x}}(-\pi/2) = \mathsf{R}_x(-\pi/2)\ \mathbf{I}$$

which connects the nD and 3D representations of the rotation group. We know that **I** is a vector and so has to transform as a vector no matter what the spin value I is. We could rewrite this as:

$$\mathsf{R}_{\mathbf{x}}(-\pi/2)\ \mathbf{I}\ \mathsf{R}_{\mathbf{x}}(\pi/2) = \mathsf{R}_x(\pi/2)\ \mathbf{I}$$

and again as

$$\mathsf{R}_{\mathbf{x}}^{-1}(\pi/2)\ \mathbf{I}\ \mathsf{R}_{\mathbf{x}}(\pi/2) = \mathsf{R}_x(\pi/2)\ \mathbf{I}$$

and we can then generalize this to an arbitrary rotation as follows

$$\mathsf{R}^{-1}\mathbf{I}\ \mathsf{R} = \mathsf{R}\ \mathbf{I} \qquad \text{// this is correct! usually written as } \mathbf{R}\mathbf{I}\ \mathsf{R}^{-1} = \mathsf{R}^{-1}\mathbf{I}$$

where $\mathsf{R}^{-1}\mathrm{I}\ \mathsf{R}$ is the normal sequence of operators one sees in talking about similarity transformations, as for example M&M page 317. Again, R is the 2x2 matrix for the rotation, and R is the 3x3 matrix.

Now, consider the effect of rotations on the density matrix. We have

$$\rho = (1/2)\ \mathbf{1} + (\mathsf{b}/2)\ \mathbf{M}\bullet\mathbf{I} \qquad \rho' = (1/2)\ \mathbf{1} + (\mathsf{b}/2)\ \mathbf{M}\bullet(\mathsf{R}\mathbf{I}\mathsf{R}^{-1})$$

as for example on page 288 where $\mathsf{R} = \mathsf{R}_{\mathbf{x}}(\pi/2)$. We can therefore rewrite this as

$$\mathbf{M}\bullet(\mathsf{R}\mathbf{I}\mathsf{R}^{-1}) = \mathrm{M}\bullet(\mathsf{R}^{-1}\,\mathbf{I}) = (\mathsf{R}\,\mathbf{M})\bullet\mathbf{I} = \mathbf{M'}\bullet\mathbf{I}$$

so that $\rho' = (1/2)\ \mathbf{1} + (\mathsf{b}/2)\ \mathbf{M'}\bullet\mathbf{I}$. We used first our result just developed, and second the fact that the dot product is a scalar so the $\mathbf{A}\bullet\mathsf{R}\mathbf{B} = (\mathrm{A},\mathsf{R}\mathbf{B}) = (\mathsf{R}^{-1}\mathbf{A},\mathrm{B}) = \mathsf{R}^{-1}\mathbf{A}\bullet\mathbf{B}$.

Therefore, when we talk as on page 288 of "rotating $\mathrm{I}_{\mathbf{z}}$ down to $-\mathrm{I}_{\mathbf{y}}$ using $\mathsf{R}_{\mathbf{x}}(\pi/2)$ sandwiched around $\mathrm{I}_{\mathbf{z}}$ as shown there, it is the same as talking about " **M** rotating from $\hat{\mathbf{z}}$ to $-\hat{\mathbf{y}}$ " , as is also shown on this same page in both equation and picture.

Now, look at the first box on page 296. The box says $\mathbf{I} \rightarrow \mathsf{R}_x(-\pi/2)\ \mathbf{I}$ in the case $\beta = \pi/2$. This is exactly our starting matrix equation above. For general β the matrix is $\mathsf{R}_x(-\beta)$ which is this matrix:

$$R_x(-\beta) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & C_\beta & S_\beta \\ 0 & -S_\beta & C_\beta \end{pmatrix}$$ // first box on page 296

We know that making the I substitutions indicated by this matrix and this box is the same as not making these substitutions and instead rotating **M** as follows:

$$\mathbf{M'} = R_x(+\beta)\,\mathbf{M}$$

As an example of this reversal sense of the sign of β, look at page 299 where (10.41) shows how you are supposed to rotate I in a certain situation (or substitute as he says). Below that shows the alternative way of thinking which is that M is rotated as shown, and you see exactly the sign change (in the sine term) that we are talking about here.

So here is the bottom line:

$$\mathbf{M}\bullet (R\mathbf{I}R^{-1}) = M \bullet (R^{-1}\,\mathbf{I}) = (R\,\mathbf{M}) \bullet \mathbf{I}$$

so that rotating **I** to $R\mathbf{I}R^{-1}$ is exactly the same as rotating **M** to R M since things appear in a dot product in the density matrix.

10.8.1 Pulse with $\phi_p = 0$. (296). Set β = 0 to see where you start, and then watch things rotate. This replacement is just the 3x3 rotation matrix $R_x(-\beta_p)$ acting on the vector I as described just above.

10.8.2. Pulse with $\phi_p = \pi/2$. (296). This rotates M around the y-axis instead of the x axis, so I_z is going to go to I_x and so on. Notice we are keeping β_p general. We have $(R\mathbf{I}R^{-1}) = R^{-1}\,\mathbf{I}$ with $R_y(\beta)$ in this case.

10.8.3,4. The cases π and 3π/2 (296) First is $R_{-x}(\beta) = R_x(-\beta)$ so the sine terms have opposite sign to the first box on the page. Second is $R_{-y}(\beta) = R_y(-\beta)$ so sine terms have signs opposite those in the second box.

10.8.5. The general case $\phi_p = \phi_p$. Malcolm does not write out the result, but says you can compute it by concatenating the three matrices shown. We rotate R_z backwards by ϕ_p to the x axis, we R_x to tip down β, then we rotate forwards again to our ϕ_p angle. This is the same as tipping down a β about the ϕ_p axis. See 9.32 where of course we apply the rightmost rotation first. He gives us the 2D representation of this rotation on page 264, but not the corresponding 3D representation which would be $R_{\phi p}(-\beta)$. Maybe he writes this out somewhere in the book.

10.8.6. Free precession for τ. We know what this does, and he writes it down in the same form as the other cases. The closing comments of this section seem obvious and results appeared earlier.

10.9 Free evolution with relaxation (298). Malcolm skips the theory and claims simply that when you take a spin system out of TE, it gradually returns, but the diagonal matrix elements (populations) restore

to TE values with one time constant T_1, while the coherences (off diagonals) fade to 0 with another time constant T_2. We know these constants have fancy names. I will skip the theory for now as well.

10.9.1 Transverse relaxation (298). If we are doing free-propagation, so to speak (no RF pulse), we know that our coherences rotate. We wedge in our little decaying exponential as shown in 10.39 and we have it! We use $\lambda = 1/T_2$. This also means we modify our little "box" so that 10.38 becomes 10.41. The equivalent form of the M rotation (with opposite sign, see above!) appears below 10.41. In free propagation, then, the projection of this M vector onto the x-y plane spirals inward as shown. Again, Malcolm is avoiding cones. His pictures would apply after a $(\pi/2)_x$ pulse since $M_z = 0$ in that case (at least until it starts relaxing). He then comments that the reason for this dephasing is just that different spins see slightly different B fields, despite our original assumption that all our systems were identical. He claims you get millions of rotations before decay really sets in with T_2. Increase entropy, no change energy. Really this is just part of thermal equilibrium just restoring.

10.9.2 Longitudinal relaxation (300). The "wedge-in" is a little more complicated here. We are saying

$$x' = x_{eq} + (x - x_{eq})\, e^{-\tau/T1}$$

so it starts out at x, and ends up at x_{eq} . Seems pretty reasonable to me.

Claim that T_1 ranges 0.1 to 100 seconds but can be much longer in certain cases.

Next, on page 301 we get a simple plot of the two diagonal ρ matrix elements over time if we do a π_x pulse and then just wait. We start at $t = -\varepsilon$ with our TE conditions for these elements. The π pulse reverses these as we have shown earlier. Then they do expo decay back to TE with time constant T_1.

On page 302 we plot the same thing but after a $(\pi/2)_x$ pulse. This pulse kills the population difference so both go to 1/2, and then we expo back to TE. Explanation of source of T_1 decay on page 302 is not so great for me. We know that the spins are going to realign eventually due to collisions imposing random TE and equilibrating rates in and out of the TE position.

Claim: theory says $T_2 \leq 2T_1$. You cannot re-align without dephasing along the way. See my rough proof of this two paragraphs below.

Practice says $T_2 \leq T_1$.

Page 303 shows our same plots of before, but shows how M_z changes. First shows the π pulse inverting things, then it restores with T_1. The second shows the π/2 pulse taking to 0 then restoring.

10.10. Magnetization vector trajectories (303). The picture page 304 shows the tip of M tracing a path just after our π/2 pulse drives it down to -y. It spirals back up. Of course to draw such a picture, you have to assume something about T1 and T2. In this picture they are equal. On page 305 top T2 is longer than T1, so the path is closer to the surface of the bounding sphere. This is right at the theoretical limit and it is sort of threatening to push through the surface of the unit sphere. The lower picture shows the reverse case where you stay deep inside the sphere. We are always in the rotating frame, by the way.

Explanation of the theoretical limit. I started but did not finish this "proof", but it seems right. As things decay, you know that $M_z = 1 - \exp(-t/T_1)$ and $M_\rho = \exp(-t/T_2)$ and we know that $M_z^2 + M_\rho^2 \leq 1$ during the decay which says the M vector cannot go outside the unit sphere.

Thus we have $f(t) = [\ 1 - \exp(-t/T_1)\ ]^2 + \exp(-2t/T_2) \le 1$ for all t in the range $(0,\infty)$. We know that $f(0) = 1$ and $f(\infty) = 1$, so the question is whether this could go negative somewhere in between. If it does, this would certainly be true at some t_o such that $f'(t_0) = 0$ and $f''(t_0) > 0$ and $f(t_0) < 0$. If we solve to find t_0 such that $f'(t_0) = 0$, we could examine either or both of the other conditions. I don't think they are both needed, so can probably just examine $f(t_0\ )$. Doing this, I was able to show that , if $T_2 \le 2T_1$, you never hit the surface of the sphere so you are OK. I showed that $T_2 \le 2T_1$ was sufficient to not hit the sphere, but I did not show it was necessary to not hit the sphere. I did not use all the information I had, and so maybe one could in fact show that [never hit the surface at any t] $\Rightarrow$ [$T_2 \le 2T_1$] .

I suspect this is really all there is to it. [I later finished this proof in spin1.doc, it is correct!]

10.11 NMR Signal and NMR Spectrum (305). I "worked through" Appendix 17.7 and have verified that (10.46) shows the complex FID signal of the form $s(t) = s_A(t) + i\ s_B(t)$ which emerges from the mixer section shown page 586. Of course the sA and sB signals are each real. Then on page 306 we rewrite this signal s(t) in "standard form" as shown in 10.47 which was used back in Chapter 5. Now, however, we have an explicit form for the constant a and involves our $\rho_$ density matrix element and two phases. The time t=0 is when the FID starts. If we factor out our complex "a" factor, then we know from Chap 5 (and I just reviewed it now) that the FT of 10.47 has the Lorentzian form shown in 10.49 where L = A + iD.

Page 307 gives an excellent summary of "how you could calculate the expected spectrum" for a FID pulse after a set of processing RF pulses. The center of the peak will be at Ω_0 which you could compute from your knowledge of γ, B^0 and δ [assuming all your spin-1/2 ensemble spins see this same δ -- otherwise it would not be an ensemble]. The width of the peak is related to T_2 which we just measure, we don't yet know how to compute this thing. The complex amplitude of the expected Lorentzian -- the complex number "a" -- is computed from the analog and digital phases you set, and from the value of the complex number $\rho_$ which you must evaluate at the start of the FID (t=0), after it propagates from a presumed initial TE value, then through your set of pulses and delays. We have explicit rules for handling any kind of pulse, and a delay.

Comments: When we draw the little icon pictures which ends with a schematized FID pulse, that FID pulse is the real voltage output by the receiving coil and it measures $\langle M_x \rangle$ as shown page 585. This is proportional to the sum of ρ_- and ρ_+ which is of course real. Remember that Faraday's Law says the voltage induces around a loop is proportional to the rate of change of the B field flux captured by the loop. This is an application of Stoke's Law page 73 Purcell where A = **E** and curl**E** = $-\partial_t$ **B** B&B p 256 and **B** = μ_o**M** if **H**=0 as on page 139 B&B. So the magnetization spinning around on its cone has an M_x component which creates a B_x field changing in time which creates our voltage by Faraday's Law. You would think they would use "lots of turns" on the detection current loop. So, we have a simple real signal FID(t) that we keep drawing in the icons.

What exactly is this real signal FID(t)? From page 585, $\langle M_x \rangle$ it is proportional to $\mathrm{Re}[\rho_-(t)]$ in the lab frame. From this same page, our FID(t) signal is proportional to $-\ 2\omega^0\ \mathrm{Im}[\ \rho_-(t)^{LAB}]$. From page 293 we know that in the rotating frame, we have that $\rho_-(t)^{ROT} = \rho_-(0)^{ROT} \exp(i\Omega^0 t)$ from 10.30. From page 285, we convert this to the lab to get

$$\rho_-(t)^{LAB} = \rho_-(t)^{ROT} \exp(+i\ [\ \omega_{ref}\ t + \phi_{ref}]) = \rho_-(0)^{ROT} \exp(i\Omega^0 t)\exp(+i\ [\ \omega_{ref}\ t + \phi_{ref}])$$

$$= \rho_{-}(0)^{\mathbf{ROT}} \exp[\, i\,(\omega_{\mathbf{ref}} + \Omega^{0})\, t + i\phi_{\mathbf{ref}}\,] = \rho_{-}(0)^{\mathbf{ROT}} \exp[\, i\,\omega^{0}\, t + i\phi_{\mathbf{ref}}\,]$$

and as expected, it oscillates at the emission frequency between the two levels. Now assume that $\rho_{-}(0)^{\mathbf{ROT}}$ has some fixed phase ε. Then we have $\rho_{-}(t)^{\mathbf{LAB}} = |\ \rho_{-}(0)^{\mathbf{ROT}}\ |\ \exp[\ i\,\omega^{0}\, t + i\phi_{\mathbf{ref}} + i\varepsilon\ ]$. We then get:

$$\mathrm{FID}(t) = -2\omega^{0}\, k\ |\ \rho_{-}(0)^{\mathbf{ROT}}\ |\ \sin(\omega^{0}\, t + \phi_{\mathbf{ref}} + \varepsilon)\ e^{-t/T_{2}}$$

where I have wedged in the decay factor and exposed an unknown real hardware constant k. So the FID signal (from a single spin-1/2 ensemble all with the same δ) is exactly an expo times the above sin going at the energy gap frequency. We don't know where to start the sine because that depends on the phases. The main information we are going to extract from this FID pulse is the number ω_{0} and the number T_{2}.

What exactly is $\phi_{\mathbf{ref}}$? It is the phase of our driving $B_{\mathbf{RF}}$ signal at time t=0 set as the start of the FID. This driving transmitter is doing $\omega_{\mathbf{ref}}\ t + \phi_{\mathbf{ref}}$ and is called "the reference". According to page 85 showing the block diagram, this phase can be adjusted by phase shifter box #2 which adds $\phi_{\mathbf{rec}}$ -- a different phase -- and this appears also on page 586. The transmitted signal is called "the reference" because it goes into the quadrature receiver as the "reference input".

Now, why not just do your FT directly on the FID(t) signal? Our FT table says:

$u(t)e^{-\alpha t}\sin(\omega_0 t)$	$\dfrac{\omega_0}{\omega_0^2 + (\alpha + j\omega)^2}$

and surely when we do our phase adjust we will get a resonance-like result with a strong peak. I suspect you could in theory do this, but the accuracy of the result would be bad because you are not taking advantage of the "differential effect provided by the quadrature mixer". If you try to do a digital FT on the real and imaginary parts of this raw signal, you have f(t) changing very fast, so you need little tiny time steps to get a result. We would much rather apply our FT hardware to a more slowly varying signal, and that is the main reason for the mixer.

What are the signals out of the mixer? If you add the two real pieces and call it a complex signal s(t), what comes out is (10.47) page 306. This signal is oscillating at the relatively low frequency Ω_{0} which is the difference between the proton resonance frequency and the transmitter frequency. Again, the two real parts of this signal are just expo-decaying sines and cosines going at Ω^{0} low frequency. This is what 10.47 says. If you FT the pulse, you get 10.49.

You don't have to "sweep" your transmitter frequency to do an NMR experiment. The pulse itself contains all the information. Of course you average lots of them to remove noise. You need to set the $\omega_{\mathbf{ref}}$ somewhere close to the expected ω^{0} so Ω_{0} is small and your FT hardware can work. Doubtless only the early time parts of the FID make real contributions to the spectrum.

10.12 Single Pulse Spectra. Here as example we look a the $(\pi/2)_{\mathbf{x}}$ pulse on page 308, and then the $(\pi/2)_{\mathbf{y}}$ pulse on page 309. We end with some quick rules showing how you can tell the nature of the real part from the nature of ρ "by inspection", nothing new here.

At this point, I read all the Notes and Further Reading references. Chapter done! This was the big payoff so far.

Question: In the quantum view the FID is caused by spontaneously emitted photons during the FID period. By what mechanism do these RF photons induce a voltage in the pickup coil? And if the coil has no load, where does the energy of these photons go?

Answer: First of all, classically, we understand that the time-dependent magnetic moments which make up M are going to radiate an EM field and that field then induces a voltage in the pickup coil. The Lorentz Force produced by the fields pushes on the electrons in the pickup wire loop.

Going the rest of the way is something I have never thought about: what is the quantized-field interpretation of Faraday's Law? The emitted photons must be absorbed by electrons in the wire and coherently push them in a certain direction. For a static wire, the Lorentz force on an electron is just $\mathbf{F} = q\mathbf{E}$ so we are faced with this simple question: suppose a photon stream going to the right has **E** field pointing up. By what mechanism does it make electrons go up in a vertical wire? The photon momentum is exactly to the right. Photon is linearly polarized.

Here is a crude answer. In some sense we know that $H' = -A^{\mu}J_{\mu} \sim \mathbf{A}\bullet\mathbf{J} \sim -\boldsymbol{\varepsilon}\bullet\mathbf{J}$ where $\boldsymbol{\varepsilon}$ is the photon polarization which we know aligns with the **E** field which in our assumed example is pointing along the wire. Therefore, "energy" would be lowered if a current were produced in the wire which flowed in the direction of the polarization $\boldsymbol{\varepsilon}$. So a force then exists trying to cause a reduction in the energy H' and that is the $\mathbf{F} = q\mathbf{E}$ force. It has nothing to do with the photon's momentum, but rather it is caused by the photon's spin polarization. So this is a crude explanation. The radiating **m** dipoles make an EM field that has an **E** vector doing something, and it is this vector which pushes the electrons and makes the Faraday current. The fact that this ends up related to time change of magnetic flux through the loop arises from Maxell's equations which relate E and B, which in turn arise from the vacuum photon equation of motion which is something like $\partial_{\mu}F^{\mu\upsilon} = 0$ which relates E and B. A very long story to be sure.