********** Part 5: Coupled Spins 1/2 **********

---------- Chapter 12: Homonuclear AX systems (339-383) ------- 44 p ---------- ###

(339) Our scenario here is as follows: we consider molecules with two spins of the same type (homonuclear, not heteronuclear), but these two spins have very different chemical shifts, so we are allowed to use the "weak coupling" approximation, see notes p233 above. Since the spins are widely separated in shift, we refer to them as A and X, so we have an AX system. An example is shown p 339 where it is the H spins that are of interest. Malcolm states the chem shift between our two H spins as 3.28 ppm, says that J_{12} is 2.9 Hz. On page 233 Eq 8.8 is the condition of weakness. We know [page 196 that $\Delta\omega = \gamma B \Delta\delta$ so we would have to show that $\gamma B \Delta\delta >> \pi J_{12}$. We know that $\Delta\delta = 3.28 \times 10^{-6}$ and $J_{12} = 2.9$ Hz. From page 14 we know that $\gamma = 267.522 * 10^6$ rads/sec-Tesla and maybe B = 5 Tesla. So we get:

$\gamma B \Delta\delta >> \pi J_{12}$??

267.522 * 10^6 rads/sec-Tesla * 5 Tesla * 3.28 x 10^{-6} >> π * 2.9 Hz ??

I am now sure about the dimensions on the right side but think I have it right. so

267.522 * 5 * 3.28 >> π * 2.9 ?? yes, by a country mile

so we really are in the "weak coupling" J-coupling situation.

Page 340 shows that each spin splits the other spin into two peaks, as we expect. It looks like the splittings might each be 2.9Hz, but we shall see. The double peaks are separated by about 650 Hz it appears. This general idea was discussed in an earlier chapter, now we are going to do the math.

12.1 Weakly Coupled Spin-Pair Hamiltonian (340) We know that Eq 12.1 is it. There is J_{12} sitting there and we express the two resonant spin frequencies in terms of their shifts. We will assume $\gamma > 0$ as it really is for H. We assume that δ_1 is the smaller chem shift. Since resonant frequencies are then both negative that means ω_2 is the more negative than ω_1. So $|\omega_1|$ is the smaller number.

12.2 Zeeman Product States and Superposition States (341). We are now going to work in the space of 1/2⊗1/2, so states are of the form | 1/2,m1; 1/2,m2> = | 1/2,m1> | 1/2,m2> (as Messiah says) but we will use the symbols α and β as before to get more compact notation. So Eq (12.3) is then a most-general superposition state, I agree. The operators need to be interpreted like this: [eg p 254 Messiah Vol I who calls this a tensor product or a Kronecker product space, I use the term direct product space]

I_{1z} really means $\mathbf{I_{1z}} \otimes \mathbf{1}$ and then

$$\mathbf{I_{1z}} \otimes \mathbf{1} \;|\; 1/2,m1;\, 1/2,m2\rangle = \mathbf{I_{1z}} \otimes \mathbf{1} \;|\; 1/2,m1\rangle\,|\; 1/2,m2\rangle = \mathbf{I_{1z}} \;|\; 1/2,m1\rangle\; \mathbf{1} \;|\; 1/2,m2\rangle$$
$$= m_1 \;|\; 1/2,m1\rangle\, 1 \;|\; 1/2,m2\rangle = m_1 \;|\; 1/2,m1\rangle\,|\; 1/2,m2\rangle$$
$$= m_1 \;|\; 1/2,m1;\, 1/2,m2\rangle$$

So all the results bottom of page 341 are trivial. The state normalization condition and vector notation on page 342 are all fine.

12.3 Energy Levels (342). What does the Hamiltonian (12.1) do to each of our four states? It is a function only of the I_z's and I might write

$$H = \omega_1^0 \; I_{1z} + \omega_2^0 \; I_{2z} + 2\pi J_{12} \, I_{1z} \, I_{2z}$$

$$= \omega_1^0 \; \mathbf{I_{1z}} \otimes \mathbf{1} + \omega_2^0 \; \mathbf{1} \otimes \mathbf{I_{2z}} + 2\pi J_{12} \, \mathbf{I_{1z}} \otimes \mathbf{I_{2z}}$$

I don't think you can write $H = H_1 \otimes H_2$ [correct], it does not factor as a direct product, that is fine. Now it does not take much to apply this to our four states and see what we get. Here we go:

$$[\; \omega_1^0 \; \mathbf{I_{1z}} \otimes \mathbf{1} + \omega_2^0 \; \mathbf{1} \otimes \mathbf{I_{2z}} + 2\pi J_{12} \, \mathbf{I_{1z}} \otimes \mathbf{I_{2z}} \;] \; | \; 1/2,m_1> \; | \; 1/2,m_2>$$

$$= (\; \omega_1^0 \, m_1 + \omega_2^0 \, m_2 + 2\pi J_{12} \, m_1 m_2 \;) \; | \; 1/2,m_1> \; | \; 1/2,m_2>$$

So our four states are eigenstates of H, that is the first obvious fact. And only the $\alpha\beta$ and $\beta\alpha$ states will have negative J_{12} terms. Remember that the first ket position is 1, the second is 2. So we now agree with (12.4). Now look graphically at the locations of the four levels! The frequencies are negative, so $\beta\beta$ is the highest in energy and $\alpha\alpha$ the lowest.

Now, $\beta\beta - \beta\alpha = -\omega_2^0$ and $\alpha\beta - \alpha\alpha = -\omega_2^0$ as well. Then finally $\beta\alpha - \alpha\beta = (-\omega_1^0) - (-\omega_2^0)$ $= |\omega_1^0| - |\omega_2^0| < 0$! But his picture shows this as positive. And all later pictures show this. Horrors, he has messed up! Errata?? Nothing said! So I will from now on assume the reverse of what he says, namely, I will from now on assume that δ_1 is the *larger* chem shift so the $|\omega_1^0|$ is larger than $|\omega_2^0|$ so the energy level pictures are then correct. [but this error really is not significant for anything that follows!]

Apart from this little issue, we see that the close states are separated just by the resonance frequencies and J_{12} only enters into the wide splittings as I show page 343 in the picture. Say this again: the numbers ω_1 and ω_2 are both negative. The upper two states have spacing $-\omega_2 + \pi J$, the lower two states have spacing $-\omega_2 - \pi J$, but J is very small. The middle two states are separated by $|\omega_1 - \omega_2| >> J$. So on the page 343 picture, J is really too small to be visible. The relative size of ω_1 and ω_2 determines which of the middle states is above the other. The states 2 and 3 could have crossed, but for his numbers they don't.

12.4 Total Angular Momenta (343). The notion of "total J" is clear to me, everything on this page is OK in this section.

12.5 Density Operator (344). Everything is fine here, but then you have to understand the box notation symbols. The diagonal ones are easy, they are probabilities to be in each of the 4 states. The off diagonals require some explanation. If the first index does not change between the two C factors, it goes into the box as the first symbol. If the first index *does* change in a manner that means left - right = +1 unit of z spin, then you put a +. For example, consider this term $c_{\alpha\alpha} \, c_{\beta\alpha}^*$. Here we have first position left - right $= \alpha - \beta = (1/2) - (-1/2) = +1$. So $\rho_{+\alpha}$. If we think in terms of a transition between states, we are saying

that in $c_{\alpha\alpha}\, c_{\beta\alpha}^*$ the left α is the final, right β is initial. Where does this come from? Consider $|\psi\rangle$ as the mix in 12.3 so that

$$\langle\alpha\alpha|\psi\rangle = c_{\alpha\alpha} \qquad \text{and } \langle\beta\alpha|\psi\rangle = c_{\beta\alpha}$$

Then $c_{\alpha\alpha}\, c_{\beta\alpha}^* = \langle\alpha\alpha|\psi\rangle\langle\psi|\beta\alpha\rangle$ which I might interpret that amplitude that state ψ links the two outer states shown. The $|\psi\rangle\langle\psi|$ is a projection operator for this state, so we have $\langle\alpha\alpha|P_\psi|\beta\alpha\rangle$. Whatever this means, I would refer to β as the initial state and α as the final, which agrees with the above notation. This thing is of course called a "coherence", later I hope to get a better interpretation for it.

If you apply a * to a coherence, you switch initial and final sense, so + $\leftrightarrow$ - in either position. This is shown in a few examples 345 top.

The two extremal coherences in the corners have order 2, double-quantum coherences. This means you have to change a state in each subspace. The order 1 coherences (single-quantum) only have to change one of the states. Here we are thinking of $\langle\alpha\alpha|P_\psi|\beta\alpha\rangle$ as some sort of transition.

So now as usual we draw an energy diagram with our four states, and a coherence is represented by an arrow going from the initial to final = right to left exactly as shown top page 346. The thing with the * on it is the initial. So as in the earlier chapters, a coherence can be represented as a directed arrow. If nothing else, this is a convenient notation. Now on page 347 he puts balls in the four states to represent four situations of pure states I guess. A bit mysterious so far.

12.6 Rotating Frame (347) Now the rotation operator here has $\mathbf{I_z}$ exponentiated, where it is the sum in the direct product sense. I now to refer back to my "matrix" section notes in the "matrix binder", which is the very last section. There I defined a certain * operator as follows:

$$\mathbf{A^*\, B} \equiv \mathbf{A} \otimes \mathbf{1} + \mathbf{1} \otimes \mathbf{B}$$

where A acts in the first space and B in the second. This is just a shorthand notation and I might call it the "compose" operator. An example of immediate interest would be

$$\mathbf{I_{1z}^*\, I_{2z}} \equiv \mathbf{I_{1z}} \otimes \mathbf{1} + \mathbf{1} \otimes \mathbf{I_{2z}} \text{ = what Malcolm just called } \mathbf{I_z} = I_{z1} + I_{z2}$$

Now it happens that α $(\mathbf{C} \otimes \mathbf{D})$ can be written either $(\alpha\mathbf{C}) \otimes \mathbf{D}$ or $\mathbf{C} \otimes (\alpha\mathbf{D})$ just from the definition of the direct product matrix, so we can write

$$\alpha(\mathbf{A^*\, B}) \equiv (\alpha\mathbf{A}) \otimes \mathbf{1} + \mathbf{1} \otimes (\alpha\mathbf{B})$$

Here is a theorem I prove in my notes:

$$\exp(\mathbf{A^*\, B}) = \exp(\mathbf{A}) \otimes \exp(\mathbf{B})$$

And therefore we would write

$$\exp(i\omega[\mathbf{A^*\, B}]) = \exp([i\omega\mathbf{A}]^*[\, i\omega\mathbf{B}]) = \exp(i\omega\mathbf{A}) \otimes \exp(i\omega\mathbf{B})$$

$$I_z = I_{1z} \otimes 1 + 1 \otimes I_{2z} \qquad \Rightarrow \qquad R_z = R_{1z} \otimes R_{2z}$$

The angle is exactly as it was in the simpler case before, involving ω_{ref} and ϕ_{ref} . Let's rotate our Hamiltonian by this thing:

$$R_z^{-1} H R_z = R_z^{-1} \{ \omega_1^0 I_{1z} \otimes 1 + \omega_2^0 1 \otimes I_{2z} + 2\pi J_{12} I_{1z} \otimes I_{2z} \} R_z$$

$$= R_{1z}^{-1} \otimes R_{2z}^{-1} \{ \omega_1^0 I_{1z} \otimes 1 + \omega_2^0 1 \otimes I_{2z} + 2\pi J_{12} I_{1z} \otimes I_{2z} \} R_{1z} \otimes R_{2z}$$

$$= \omega_1^0 I_{1z} \otimes 1 + \omega_2^0 1 \otimes I_{2z} + 2\pi J_{12} I_{1z} \otimes I_{2z}$$

= H // so nothing happens at all for this particular Hamiltonian

Now let's assume that (12.8) page 349 is true as the transformation of a Hamiltonian from a lab to a rotating frame. The derivation of this back on page 255 was pretty general. Then (12.8) gives:

$$R_z^{-1} H R_z - \omega_{ref} I_{1z} * I_{2z} = H - \omega_{ref} [I_{1z} \otimes 1 + 1 \otimes I_{2z}]$$

$$= (\omega_1^0 - \omega_{ref}) I_{1z} \otimes 1 + (\omega_2^0 - \omega_{ref}) 1 \otimes I_{2z} + 2\pi J_{12} I_{1z} \otimes I_{2z}$$

$$= \Omega_1^0 I_{1z} \otimes 1 + \Omega_2^0 1 \otimes I_{2z} + 2\pi J_{12} I_{1z} \otimes I_{2z}$$

as shown. Same as original Ham but $\omega \rightarrow \Omega$ in the two obvious places.

Before going into the rotating frame, we had our Hamiltonian 12.1, and our states were eigenstates, so the Hamiltonian was diagonal and the four diagonal elements were the eigenenergies shown on page 343 and which we plotted in the picture. Now in the rotating frame, we have rotating eigenstates I suppose with twiddles on them, and the energies are now as in 12.10. He finally shows this at the bottom of page 349.

12.7 Free evolution (350). How does our ρ matrix "evolve" with no applied RF pulse?

12.7.1 Evolution of a spin pair (350). I presume this state $|\psi>$ is now in the rotating frame and the coefficients are the mix in the rotating frame of the rotating frame direct product eigenstates. So let's quit saying this all the time. He writes the SE. We know the free-precession propagator is the exponentiated Hamiltonian as usual, and the exp of a diagonal matrix is a matrix with expo diagonal elements. I don't think Levitt proved this, easy to prove on paper, I just did it. So the conclusion is that with no applied pulse, we get our coefficients just "phasing along" at their respective eigenfrequencies as shown top 351. So in this section, we have just watched how the little 4-vector propagates.

12.7.2 Evolution of the coherence (351). If we think of a coherence as for example $\rho_{\alpha+} = c_{\alpha\alpha} c_{\beta\alpha}^*$ without averaging for the moment, then we can insert the propagations we just got in the last section. We then get

$$c_{\alpha\alpha} c_{\beta\alpha}^* \text{ (at time 3)} = c_{\alpha\alpha} c_{\beta\alpha}^* \text{ (at time 2)} * \exp(-i\Omega_{\alpha\alpha}\tau) * \exp(+ i\Omega_{B\alpha}\tau)$$
$$= c_{\alpha\alpha} c_{\beta\alpha}^* \text{ (at time 2)} * \exp(-i[\Omega_{\alpha\alpha} - \Omega_{B\alpha}] \tau)$$

so the "states" in my example are r = αα and s = βα. This then looks like Eq 12.11. Now when we average over the ensemble, the expo acts like a constant since the energy levels are constant in the ensemble, it is just the coefficients that are different in different states of the ensemble. It is a mixed state.

At the bottom of page 351 he does another example which I agree with. He has defined a phasing frequency for each coherence element (really for each matrix element of ρ and of course the diagonal elements don't change! There are no transitions yet. (he has not yet said all this). So give each coherence a frequency using the same "box notation". There are 16-4 = 12 off diagonal elements, and he purports in 12.12 to state the frequency for each element. I checked all of these, so now we know how each coherence in box notation changes in time. We can add an expo decay λ as shown middle page 352 if we like, pretend same for all ρ elements. // Remember: these things in 12.12 called Ω-- for example are just the free-propagation phases of the various ρ_{nm} matrix elements.

Note added 1.24.08. The discussion is very convincing in showing that the $c_{\alpha\alpha}$ objects move in time according to the top of page 351. This is just the usual $|\psi(t)\rangle = \exp(-iHt)|\psi(0)\rangle$ where H is diagonal and ψ is a 4-vector and $H = +\Omega^0 I_z$. So the second conclusion is also convincing as quoted above, such as

$$c_{\alpha\alpha}c_{\beta\alpha}^*(t) = c_{\alpha\alpha}c_{\beta\alpha}^* (0) * \exp(-i[\,\Omega_{\alpha\alpha} - \Omega_{\beta\alpha}]\, t)$$

(a) The first question is this: how is this thing related to the "box notation" ? Well, first of all, we certainly know that $\langle\alpha\alpha \mid \rho \mid \beta\alpha\rangle = \rho_{+\alpha}$ because we have raised β to α. Now we also know that:

$$\langle\alpha\alpha \mid \rho \mid \beta\alpha\rangle = \langle\alpha\alpha|\psi\rangle\langle\psi|\beta\alpha\rangle = c_{\alpha\alpha}c_{\beta\alpha}^*$$

which agrees with Malcolm's picture (my red arrows). So, when we "look at" something like $c_{\alpha\alpha}c_{\beta\alpha}^*$, we know this is a $\rho_{+\alpha}$ and we think of the second factor $c_{\beta\alpha}^*$ as being the "state on the right". [So in part (a) here we have no contradiction with Levitt.]

(b) Next, let's look at the exponential. We *define* quantity $\Omega_{+\alpha} = -[\Omega_{\alpha\alpha} - \Omega_{\beta\alpha}]$ to include the minus sign in the phase (shown page 352), so then we end up with:

$$\rho_{+\alpha}(t) = \rho_{+\alpha}(0) \exp(+i\Omega_{+\alpha}t)$$

This certainly implies that

$$\rho_{-\alpha}(t) = \rho_{-\alpha}(0) \exp(-i\Omega_{+\alpha}t)$$

but when we write this, we will use $\Omega_{-\alpha} = -\Omega_{+\alpha}$ so we get

$$\rho_{-\alpha}(t) = \rho_{-\alpha}(0) \exp(+i\Omega_{-\alpha}t)$$

So, using the full box notation, the exponent *always shows a plus sign* for either + or – coherences!

So, with this *definition* of the frequency associated with the coherence label, we get a + sign in the exponent. You see these for example on page 353. We want plus signs because that is what we assumed for the sign when we did our FT back on page 98 bottom. If the phase has a + sign, then the pole will be at the number you see, and this is shown on p 102, and is a consequence of the fact that FT(e^{+iat}) puts the pole at $\omega = a$.

Notice that , from energy level diagram page 343, that $\Omega_{+\alpha} = \Omega_{\beta\alpha} - \Omega_{\alpha\alpha}$ is a positive number. So in our + coherence, we have a positive sign and a positive number in the phase.

This seems confusing because, as noted above, back on page 292 we found that a + coherence should have a *negative* sign in the exponent and the number there was Ω_0. But of course this number Ω_0 is negative. In other words, suppose back on page 292 we had defined $\Omega_+ = -\Omega^0 > 0$. Then for (10.30) we would have that $\rho_+(t) = \rho_+(0) \exp(+i\Omega_+ t)$ where $\Omega_+ > 0$. And we would define $\Omega_- = -\Omega_+$ and then we would say that $\rho_-(t) = \rho_-(0) \exp(+i\Omega_- t)$ where now $\Omega_- = \Omega^0 < 0$.

So the answer is this: we always define the "box notation frequency" so that the exponent has a + sign, and this is what we want for Fourier Transform purposes.

12.8 Spectrum of the AX system: the spin-spin splitting (352). The opening claim is that the NMR signal is driven by the sum of the four coherences which have a single minus sign in them! This is not at all obvious to me, even having read that appendix [but see separate notes The Density Matrix.doc where I show that the sum of the four terms is correct in Part V] . But in a quantum point of view I know that each of these terms represents a possible photon absorption from the RF pulse and these are shown as the arrows on page 354. These transitions then decay back down and emit the photons which are picked up by the coil and that gives us our four "lines". If we go back to page 343, and if J_{12} is very small compared to our $\omega 1 - \omega 2$ gap (this is, after all, what page 341 requires), then the lines that will be very close are $1 \rightarrow 3$ and $2 \rightarrow 4$ and the other similar pair. This is what you see page 354 where each picture shows a signal of J_{12} case. In general, the splittings are separated by $2\pi J$, while the two pairs are separated by $\omega 1 - \omega 2$. For the other sign of J, the peaks in each close pair just swap. Page 353 shows the time-dependent signal contributions, and then the Fourier Transform, and the a-values. We are all done. The energy level pictures are shown on the next page.

Now let's pause to think about where the Ω guys are located as shown page 349. If, as he says back on page 341, $\delta_1 < \delta_2$, then from center page 349 we have $\Omega_1 - \Omega_2 = \gamma B^0 (\delta_2 - \delta_1) > 0$, so Ω_1 should be to the right of Ω_2 and that is shown correctly in the page 354 pictures. But δ_1 smaller means that ω_1 has the smaller abs value, and this does agree with $\omega_1 > \omega_2$ for these negative numbers, just as he says on page 341. But I still get $\omega_{\beta\alpha} - \omega_{\alpha\beta} = -\omega_1 + \omega_2 = (-\omega_1) - (-\omega_2) = |\omega_1| - |\omega_2| < 0$ in disagreement with the picture on page 343.

Let's now look in the rotating frame on page 349. The signs of the relative frequencies are less clear than before. Suppose we take ω_{ref} lying at 0. Then I did it and get my same conclusion.

I think the fix is this: all equations and claims are correct, but in all pictures one should have drawn the $\alpha\beta$ state a little above the $\beta\alpha$ state instead of the other way around! This I think fixes everything, except then his page 355 pictures are wrong and his errata pictures don't fix them! I have done my own edits on the top picture, he has moved all the states around, very confusing indeed.

At this point, I paused and wrote up **two docs and sent them to Malcolm**. He replied at once, but said his second edition is imminent so none of my fancy stuff could get added, probably a pat line he gives

people. He was just sending an ACK and later I will hear back I think. // He later said he read my spin2 and maybe we will meet some day, and his 2nd Ed is imminent.

Comment on the page 354 figure. There are four peaks. I have shown the expected location of each peak. Here they are:

$-\beta$	$\Omega_1^0 - \pi J$	splitting between these peaks is $2\pi J$
$-\alpha$	$\Omega_1^0 + \pi J$	
$\beta-$	$\Omega_2^0 - \pi J$	
$\alpha-$	$\Omega_2^0 + \pi J$	

12.9 Product Operators (355)

12.9.1 Construction of product operators (356) Here is an explanation of the graphical method used here:

	1/2,1/2	1/2,-1/2	-1/2,1/2	-1/2,-1/2
1/2,1/2			|	
1/2,-1/2			|	
-1/2,1/2			|	
-1/2,-1/2			|	

This is how the 4x4 matrices are labeled. If we have $A = A^1 \otimes A^2$, then in the upper left quadrant, all four matrix elements have the common first factor $(A^1)_{1/2,1/2}$ and the $(A^2)_{a,b}$ have the "normal order" for our 2x2 matrices. Similarly, in each quadrant we have a common element for A^1, and in fact these common elements themselves form a normally ordered matrix spread farther apart, and we of course end up exactly with the construction Levitt shows. Fine by me!

Here is a little more on this subject. Suppose we thought of $\alpha = 0$ and $\beta = 1$ as labels. Then a direct product matrix looks like this:

$[AxB]_{ai,bj} = A_{ab} B_{ij}$

bj→

ai ↓	0,0	0,1	1,0	1,1
0,0	ab=0,0		ab=1,0	
0,1				
1,0				
1,1				

The upper left square has ab = 00 so has a constant factor A_{ab}. You multiply this by B_{ij} to fill out that upper left square. This shows that the 4x4 matrix is four copies of B_{ij} weighted by A_{ab} in this manner. With this state ordering, it only works this way, you cannot switch the roles of A and B!

Page 357 examples:

$I_{1x} \otimes I_{2z}$ = as shown $1 \otimes I_{2y}$ = as shown

12.9.2. Populations and coherences (358) . Let's look back at the density matrix on page 344. Think of the labels along the top and sides being like those shown above. Here I will do it again. Think of the top as the initial. So if top→left has β→α, then m increased by 1, so we get a + sign.

	α,α	α,β	β,α	β,β
α,α	αα	α+	+α	++
α,β	and so on			
β,α				
β,β				

The + and - signs merely say that a particular S_z quantum number is changing by 1. But I am still hazy about what an element of this matrix means. [See Density Matrix separate document.]

Now I think we have another Levitt error: He draws the correct I_{1z} matrix, but now we are confused about how the states should be labeled on the diagram. Which sign of γ is he now assuming? The H spin has $\gamma > 0$ and page 339 says we are working with H atoms, so lets assume $\gamma > 0$. But this does put ββ at the top of the diagram, and this means ω's are negative as on page 340, and this means ββ has the highest positive energy. I see in his later pictures that β arrows are connecting to the top state, so that must be right.

So he has goofed up on page 358. If ρ contains a positive I_z term, then I would say the top two states should not be depleted but should be enhanced. So I think the words are wrong, and the picture is also wrong. The two top levels should have the darkened balls. And I don't know about the ordering of the two middle levels here, it just continues to be wrong I think.

Now at page bottom page 358, for that term he has the balls done right, and he is correct to say that the two central states are depleted.

So, Example 1 on page 358 has this error. Example 2 is correctly done. Example 3 is like the I_x example I consider in my Density Matrix notes and this kind of matrix would be made by an RF pulse and you then will have photon transitions as he shows.

I think I am now happy with all of this section, including the following identification of non-zero coherences from the from of terms in H'.

12.9.3 Spin Orientations (361).

Example1: Remember that $\langle M_{1z} \rangle \sim \langle I_{1z} \rangle = \mathrm{tr}(\rho I_{1z})$. Remember also that if you square any of the I component 2x2 matrices shown on page 164, you get 1/4*1 which we can just write as $I_i^2 \sim 1/4$. In the direct product space, then we would have $(I_{1z} \otimes 1)^2 = 1/4 \; 1 \otimes 1$. Now, suppose ρ contains a term of the form $+3 I_{1z}$. Then we get $\langle M_{1z} \rangle \sim \langle I_{1z} \rangle = \mathrm{tr}(3 I_{1z}^2) = 3/4 \; \mathrm{tr}(1) = 3$. So we can argue that a positive I_{1z} term in ρ is associated with a positive $\langle M_{1z} \rangle$ and this then justifies the picture shown on page 361 bottom. Why does author fail to make this simple point?

Example 2: Same idea but I_{2z}.

Example 3: Same idea but I_{1x}.

Example 4: Here he does $I_{1z}I_{2z}$. Again, square this and get 1. But this is now $\langle M_{1z}M_{2z}\rangle$ = positive number, say. This then agrees with picture bottom page 362. Could both be positive or both negative to contribute a positive result.

Example 5: Same idea but $I_{1x}I_{2x}$.

OK, I am happy with all this, but I question his identification of specific "coherences" with these matrix patterns, since coherence = a number, and the patterns he shows are matrices. Save for later.

12.10 Thermal Equilibrium (364). Very straightforward section, and we get a TE starting 4x4 matrix as shown top page 366. This assumes large B_0 and high temperature, as usual.

12.11. Apply the RF pulses! (366). As usual, the RF pulse produces the I_x and I_y mixture in the Ham.

12.11.1. Effect of pulse on a state (367). We do the SE and the expo Ham with the usual triple rotations. We have product of 1 and 2 rotations now, that is the difference. For the first time he writes the triple matrix product at page 368 top, and then converts this to 4x4 in the usual manner. We then look at the special case of the $\pi/2$ pulse. We see that it takes the $\alpha\alpha$ state and throws it into a complete mix of all four states. In the simpler spin-1/2 case a similar thing happened, we started in α and got a mix of α and β when we "knocked z down to -y".

12.11.2 Effect of pulse on matrix ρ (368). I believe the results here, but I think it is MUCH easier to work in the direct product notation and avoid 4x4 matrix altogether. Then we just replicate our simpler spin-1/2 case in each subspace, and we get the result shown on page 369 "by inspection". The second example also follows by inspection, though we have no idea how you would get such a term in ρ. Certainly not from a $(\pi/2)_x$ pulse. But he is just showing that you do the intuitive thing in each of the subspaces to get the result.

12.11.3. Operator transformations (371). Here he does what I just said. Work separately in the two subspaces. Use the sandwich formulas to do rotations, reach conclusions like that shown page middle, avoid all those 4x4 matrices. Use the graphical method in each subspace. Page 372 shows the effect of the $(\pi/2)_y$ pulse in the #1 subspace, then says it is same in the #2 subspace. Fine.

12.12 Free Evolution (ie, no pulse) (373). The situation is this: we have our H^0 Hamiltonian with its three z-terms as shown in the box page 349, the last term being $\pi J_{12}(2I_{1z}I_{2z})$. We need to "expo this Ham" to get our free-space motion. So Malcolm suggests to just do it in three steps, in any order you want, since everything commutes with everything here, see page 374. But we don't actually do these rotations yet.

12.12.1 Chemical Shift Evolution (375). This means let's do the two simple parts and save the J_{12} part for later. The two linear I terms control the chemical shift, hence the name here. We know that these rotations are as shown page 375 for the #1 case, and similar for I_2 . So, on page 376, he applies the pair of rotations first to I_{1x} and then to $(2I_{1x}I_{2y})$. Nothing fancy here, though the result is a bit messy. The duration of propagation is τ, as usual. We are in the rotating frame so see Ω stuff. Notice that the first thing makes single I results, but the second thing makes all double-I results, known as correlations. He is not yet telling us why these two examples will be of interest.

12.12.2 J-Coupling Evolution (376). Now remember that $(2I_{1z}I_{2z})$ is what sits in our J_{12} term which we want to exponentiate. We have a sneaky way to do this. First, you trivially derive the commutators in (12.25) which are really "true by inspection". You realize each is cyclic for obvious reasons. So we are going to treat $(2I_{1z}I_{2z})$ as the "A" of the sandwich formula on page 144. We have to know what B and C are, and that is what the commutators and pictures below tell you. In fact we have four different triples here, four pictures, four commutators. The expo Ham angle is πJ_{12}. So, if we do our expo Ham sandwich as shown top page 378, we get the result shown. The "singleton" term I_{1x} is a linear combination of itself and a "doublet" term. This time he does to different cases as "examples". The labeled arrow notation is faster than showing the rotation expo Ham all the time. Then on the bottom of page 378 he "does" two more examples. Each example gets a full-bore picture set to go with it.

Things then get a little strange. First, we get some commutators that are zero. The last four of the set of 8 are not as obvious as the first four, but I will defer deriving them until the end of this section. Notice that the first term in each commutator is our $H' = \pi J_{12}(2I_{1z}I_{2z})$ Ham term. If a commutator is 0, then the expo Ham sandwich of H' is doing to do nothing at all! So certain bilinear I combinations don't change over time. An example is $I_{1y}\, I_{2x}$.

At this point, we get the mysterious italic statement top of page 380. There seems to be no connection at all between the words in the statement and what he has just shown. So let's look back at page 361 where he examines a 1y-2x term. He writes this in raise/lower notation, and then we see that whenever you have a combination like this, you get something like $I_1^+ I_2^-$. He makes a claim there that the coefficient of this is the ρ_{+-} coherence! How do we know that??? Well consider:

$$\langle \alpha\beta \mid I_1^+ I_2^- \mid \beta\alpha \rangle = \text{the only nonzero matrix element of this operator product.}$$

Imagine there is such a term like $3I_1^+ I_2^-$ sitting in the ρ expression. Then in this example, the above matrix element is in the second row (the bra) and the third column (the ket). That is the element Malcolm wants to call ρ_{+-} . Fine. We could then associate $\langle \alpha\alpha \mid I_1^+ I_2^+ \mid \beta\beta \rangle$ with the first row, last column, ρ_{++}. Then suppose we have I_1^+ all by itself. Then we get $\langle \alpha\alpha \mid I_1^+ 1 \mid \beta\alpha \rangle$ = 1st row, 3rd col = $\rho_{+\alpha}$ and this also agrees. And of course for the same operator we have $\langle \alpha\beta \mid I_1^+ 1 \mid \beta\beta \rangle$ = 2nd row, 4th col = $\rho_{+\beta}$.

So we have a "naming theorem" here that he neglected to derive for us.

Coherence Naming Theorem: The coherence ρ_{AB} is the matrix element of the operator $I_{1A}I_{2B}$ with the following rules:

(1) if neither A nor B is a sign, then ρ_{AB} is the diagonal element that AB indicates, and these coherences are called populations. The operators appearing in ρ are any combinations of I_{1z}, I_{2z} and 1 because these operators only have diagonal matrix elements.

(2) if exactly one of A and B is a sign (call it s), then operator possibilities must have an I^s for the one associated with the sign, and the other operator is 1 or I_z . We are raising or lowering just one of the spins in this case. These cases are shown in the top four pictures on page 348.

(3) if both A and B are a sign, then we have the corresponding pair of operators $I^{s1}\, I^{s2}$ and then both spins are making a change in the non-zero matrix element. If signs are different, you get the second last picture cases, otherwise the last case.

Now, if you see something like $I_{1x}I_{2z}$ you expand I_{1x} into its + and -, and this is then case (2) where one of the spins is changing and the other is not. This is generally the case when we have a combination

let's just call I_{1t} I_z or just I_{1t} where t = transverse = x or y. Now if you have I_{1t} $I_{2t'}$ such as $I_{1x}I_{2y}$, then you are talking about double signed things (++, +-, and so on).

Now finally we come back to page 379. The expo Ham of the J-coupling puts $I_{1z}I_{2z}$ on the two sides, and you use this on a ρ which is in the middle of the sandwich. If we have a ρ term of the form I_{1t} $I_{2t'}$, we know that "nothing happens" in the sandwich, the breads just cancel each other because the commutators are all zero. He shows all four cases of I_{1t} $I_{2'}$ in the last two lines of (12.26). Since these terms are associated with the double-signed ρ elements, we now agree with his claim at the top of page 380 that J-coupling has no effect on the double or zero quantum coherences. You see an example of this right away on this same page at the start of the second arrow set. There, $\pi J_{12}\tau$ rotates a term of the form I_{1t} $I_{2t'}$ into itself, that is, it "does not evolve".

So, now this page gives the evolution of two example "ρ terms" as shown. Remember you might as well do them in whatever order seems easiest. In the first example, you see that I_{1x} (which we now know to call a single-quantum coherence term, a ρ having one sign) evolves into the same class of object, probably shuffling things around within this class. The second example shows a double-quantum / zero-quantum class object $I_{1x}I_{2y}$ (of our form I_{1t} $I_{2t'}$) being expo-Ham'd into objects of its same class. The J_{12} cannot evolve these, but when you throw in the other two rotations, you get evolution. So everything moves in the general case! But things stay in their class.

12.12.3. Relaxation (381). Without proof he claims that the "z combinations" of operators, which we associate with the diagonal ρ elements or populations, have complex relaxation situations and we get to this eventually in Chap 16. But the off-diagonals can be handled with a single decaying expo.

You need to keep in mind that between pulses when we "free propagate" the density matrix ρ, in fact you are getting "relaxation" occurring, but Malcolm ignores this in his pulse gaps, the justification is not given at this point for doing this. Obviously this means the free-periods are << than T_1 and T_2.

12.13. The Spin Echo Sandwich (SES) (381). I am getting hungry. Our proposed pulse sequence is as shown page 381, and the correct ρ propagation operator is then the product of the three rotations shown top of page 382. The two outer ones are free evolutions, the middle is a π_x pulse.

The SES Theorem (proven in a 7-page appendix!): In appropriate conditions, if you slide the π pulse to the left, then in the double-sized τ evolution that then exists on the right side of the π_x pulse, the system propagates *as if* ONLY the J couplings were operational. So notice in 12.27 that U_{12} appears, not the full U. This certainly is a simplification!

Now, suppose you know the value of πJ_{12} for your particular AX system and you set $\tau = 1/2J_{12}$ so that the angle in the J_{12} propagator is $\pi J_{12}\tau = \pi/2$. For such a pulse, the claim is that you get the upper list of results shown on page 383. How would I prove these claims are correct? I think I know the answer. Look first at page 377 bottom figure (a). Suppose you rotate π/2 about the "a" axis. If is pretty obvious what that does to the other two vectors, and these are the first two of our 8 conditions. Then figure (b) gives the next two. Fig (c) , and so on, so all done in about 30 seconds.

Now, what does the π_x pulse do? What do we mean by such a pulse in this 2-spin context? Well, it means the product of the 1 and 2 rotations, as shown middle of page 367. So this then makes all the π_x

rotations shown on the left side of page 383 quite obvious, and we then have a list of the effect of a tuned SES pulse on all 8 operators shown. Not clear yet why this list has the ones we care about.

Now we get another "mystery statement" from Malcolm. What exactly is an "uncorrelated spin state"? I guess it is when you have just a single I_{1t} type term in ρ, it is turned into a product term. In the earlier pictures, the double I terms were shown to imply correlations between the two spins, so fine. So if had your spin ensemble in some kind of correlated state, you can move it to a simpler single-I operator state with one of these tuned SES pulses.

End of chapter!

Some Pauli Matrix Theorems and notes on the commutators in (12.26).

The I's are related to the Pauli σ matrices as follows: $\mathbf{I} = 1/2\ \boldsymbol{\sigma}$

Here is a little theorem that you can prove in about 2 minutes using the Pauli fact that

$$\sigma_i\sigma_j = i\varepsilon_{ijk}\sigma_k + \delta_{ij}\,1$$

Theorem 1:

$$[\ \sigma_i\,\tau_\ell,\ \sigma_j\ \tau_m\ ] = 2i\ \{\ \delta_{ij}\,\varepsilon_{\ell mn}\tau_n + \delta_{\ell m}\,\varepsilon_{ijk}\,\sigma_k\ \}$$

where σ is Pauli in the 1 space, and τ is Pauli in the 2 space. You prove this by just writing it out and using the little Pauli product rule.

So here are some examples:

$[\ \sigma_3\,\tau_3, \sigma_1\ \tau_1\ ]$: $\delta_{ij} = 0$ and $\delta_{\ell m} = 0$ so get 0.
$[\ \sigma_3\,\tau_3, \sigma_1\ \tau_2\ ]$: same conclusion exactly so = 0.
$[\ \sigma_3\,\tau_3, \sigma_2\ \tau_1\ ]$: same conclusion exactly so = 0.
$[\ \sigma_2\,\tau_3, \sigma_1\ \tau_2\ ]$: same conclusion exactly so = 0

So this quickly proves all four of the cases that are the last four in 12.26. These results are specific to the j=1/2 representation of the SO(3) generators!

Here is another theorem of interest:

$$[\ \exp(-i\theta\sigma_i), \sigma_j\ ] = \Sigma_n\,(-i\theta)^n/n!\ \ [\ \sigma_i{}^n\ , \sigma_j\ ] = \Sigma_{n\ \mathrm{even}}\,(-i\theta)^n/n!\ [\ 1, \sigma_j\ ] + \Sigma_{n\ \mathrm{odd}}\,(-i\theta)^n/n!\ [\ \sigma_i\ , \sigma_j\ ]$$

here the last steps arise because $\sigma_i{}^2 = 1$, which is only true (I imagine) for the 2D representation of the Lie generators. We then get:

$$= \Sigma_{n\ \mathrm{odd}}\,(-i\theta)^n/n!\ [\ \sigma_i\ , \sigma_j\ ] = \Sigma_{n\ \mathrm{odd}}\,(-i\theta)^n/n!\ \ 2i\varepsilon_{ijk}\sigma_k = 2i\varepsilon_{ijk}\sigma_k \qquad \Sigma_{n\ \mathrm{odd}}\,(-i\theta)^n/n!$$

and then

$$i \Sigma_{n\ odd} (-i\theta)^n/n! = \Sigma_{n\ odd} (\theta)^n/n! \ * \ i * (-i)^n$$

The first term has $i * (-i)^n = i * (-i) = +1$. The next term is -1, and signs alternate, so we have

$i \Sigma_{n\ odd} (-i\theta)^n/n! = \theta - \theta^3/3! + \theta^5/5! - .... = \sin\theta$. Therefore we have shown that

$[\exp(-i\theta\sigma_i), \sigma_j] = 2 \sin\theta \ \varepsilon_{ijk}\sigma_k = [R_i(\theta),\sigma_j]$

This is a result I have never seen before, I should add it to my Pauli page. So here we can summarize:

Theorem 2: $[R_i(\theta),\sigma_j] = 2 \sin\theta \ \varepsilon_{ijk}\sigma_k \Rightarrow [R_i(\pi/2),\sigma_j] = 2 \ \varepsilon_{ijk}\sigma_k$ and $[R_i(\pi),\sigma_j] = 0$

This last result has the implication in Levitt that $[R_i(\pi),I_j] = 0$ such as $[R_x(\pi),I_z] = 0$. It then follows that:

$[R_x(\pi), I_{1z} I_{2z}] = [R_{1x}(\pi) R_{2x}(\pi), I_{1z} I_{2z}] \Rightarrow$

Here, each operator is in the direct product space. If we use the usual [AB,CD] formula, each term is zero because the commutator of each pair of terms vanishes. This is either because (1) they are in different subspaces, or (2) due to our rule that $[R_i(\pi),I_j] = 0$ with a subspace. Therefore:

Corollary:

$[R_x(\pi), I_{1z} I_{2z}] = 0$ // in the spin-1/2 representation only of the I matrices.