Appendix 17.12 Chemical Exchange PhL 3.25.08→3.26.08

An example of the situation described here is shown top of page 481 where we have two CH_3 groups which can exchange (non-equivalent positions) in a molecule. We know that if there were no exchange, the H's in each group would have some δ and you would get a spectrum with two distinct lines. The question is this: what happens to this spectrum if exchange occurs at some average rate k ? You might expect that if the exchange happens super fast, you might only get one broader line. In this appendix, we make a simple math model for what happens here.

In the opening section of this appendix, we define our situation and refer to the two molecular states as type A and type B, the H's in the two CH_3 groups just mentioned, for example. Each has a different local environment, so each type has a distinct density matrix called ρ_A and ρ_B. For example, ρ_A describes an ensemble of systems but looks only at the A H's in those systems.

17.12.1 The Incoherent Dynamics. The assumption is that the change is instant, and occurs randomly, and there is some average rate and he says this is a Markov process assumption. The top equation on page 629 describes how the A system loses a population at rate - k ρ_A but gains it at rate k ρ_B. In fact, you can apply this equation to the entire ρ_A matrix or operator because A's are leaving and new A's are arriving. In this way, we arrive at (17.76) describing $d\boldsymbol{\rho}/dt$ as a function of $\boldsymbol{\rho}$, where $\boldsymbol{\rho}$ is a 2D vector (A,B). This "term" on the RHS is due to the flow back and forth between A and B, and this is called the "incoherent" contribution to the $d\boldsymbol{\rho}/dt$. We are interested mainly in the matrix element (and 2D vector) $\boldsymbol{\rho}_-$.

17.12.2. The Coherence Dynamics. Were there no exchange, we know that each ρ_- just "phases along" with its own Ω_A or B as shown. This leads to the diagonal equation (17.77).

********** this is a very long section **********

17.12.3. The spectrum. So obviously we want to add the two components of the $d\boldsymbol{\rho}/dt$ and we end up with (17.78) which is written in terms of a 2x2 matrix he calls L.

At this point, I will wander off with my own description of things.

First, **our problem here** is to solve for $\boldsymbol{\rho}(t)$, a 2D vector. We expect to see some oscillatory signals here, perhaps two, and we will know the time domain result, and we can then figure out from that the *spectrum* which is the title of this section.

A. Review of solving the SE.

Now, let's digress to think about the Schrodinger Equation SE. We have a TI and TD version of this equation, namely

$$H\phi_n = E_n\phi_n \qquad\qquad H\psi = +\, i\, d\psi/dt$$

From the second equation, if H itself is time-independent, we solve to get

$$\psi(t) = e^{-iHt}\,\psi(0)$$

and this gives us a formal solution of the SE for $\psi(t)$. If it happens that H is a 2x2 matrix, then we are faced with the **technical problem of exponentiating a 2x2 matrix**. If the matrix H were diagonal, this exponentiation is trivial, but if it is not diagonal, you have a problem on your hands. In what follows, we learn a "trick" for, in effect, doing this exponentiation of a matrix.

In the case of a Hamiltonian, we know we can find a 2x2 unitary matrix X such that

$$X^{-1} H X = H_d \qquad = \text{a diagonal matrix}$$

We formally know this is possible because H is Hermitian. We also know that one possibility for the matrix X is the matrix whose columns are the eigenvectors of H. That is, $X = \{ \phi_1, \phi_2 \}$ in the N=2 case. If the eigenvalues are distinct, this is especially simple. If they are not, we may have to fiddle with GSO to come up with linearly independent eigenvectors, but we can ignore that in our present example.

Suppose then that we "go off" and we solve the TI SE in our case of interest, and we find the values of E_n and of ϕ_n. Then we will have found an X which brings H to diagonal form. Assume that we have done this in our 2x2 case. We can then conclude without much effort that

$$X^{-1} e^{-iHt} X = e^{-iHdt} = \text{a diagonal matrix} = \text{diag}(e^{-iE1t}, e^{-iE2t})$$

by just sandwiching the X's around each term in the expansion for e^{-iHt}.

Now, this leads us to a closed form solution for $\psi(t)$ which is what we are after in our study of the TI SE. We have

$$\psi(t) = e^{-iHt} \psi(0) = X e^{-iHdt} X^{-1} \psi(0)$$

Since we have solved the TDSE, we know all three matrices shown on the right and we then just multiply things out and we have our solution $\psi(t)$. This method of course applies for any dimension H we want, not just N=2, and surely also for $N=\infty$ as would arise in continuous spectrum situations.

<u>B. Applying the above to the current application.</u>

$$L\phi_n = d_n\phi_n \qquad L\rho = d\rho/dt \qquad \rho(t) = e^{Lt} \rho(0)$$

Our "TDSE" here lacks the -i we had in the true TDSE, and so this -i is also missing from the exponential formal solution to the problem shown on the right. The TISE looks the same The functions here are all 2D vectors, I have bolded them but Gk letters are hard to see bolded in my font. We know the solution on the right is correct because we can apply d/dt to it, to get the TDSE in the middle, and as before, we assume that L is itself not a function of time. So, our technical problem is "how to compute e^{Lt}" so we can write down our solution $\rho(t)$ in a closed and useful form. I have called the eigenvalues d_n instead of E_n.

We could make this problem look just like the real SE problem by defining -iH = L or H = iL. However, H so defined would not be Hermitian (much less real symmetric), so we expect that our eigenvalues won't be real (they are complex). So in our little SE analogy, we cannot use "matrix theorems" which relate to Hermitian matrices.

Nevertheless, we have some matrix theorems which are useful. In my matrix binder, the first theorem of interest is Theorem 15D in the "2 section" (page 18) which says this: if you have already solved the TI

SE problem and know the eigenvectors and eigenvalues, then you can write $LX = XL_d$ which merely groups things and says that $L\{\phi_1, \phi_2\} = \{d_1\phi_1, d_2\phi_2\}$ which is just a restatement of $L\phi_n = d_n\phi_n$.

Next we have Theorem 15E following which says the obvious: if it happens that $\det X \neq 0$, then we know we can compute X^{-1} and then we have $X^{-1}LX = L_d$. Then we have shown that our matrix of eigenvectors X is a candidate similarity for bringing L to diagonal form. In our current example this will turn out to be the case, and we can then go on to solve our problem as follows:

$$X^{-1}LX = L_d \qquad \Rightarrow \qquad X^{-1}e^{Lt}X = e^{Ldt} = \text{diag}\,(e^{d1t}, d^{d2t})$$

$$\rho(t) = e^{Lt}\rho(0) = X\,e^{Ldt}\,X^{-1}\rho(0)$$

which is what Malcolm says in his equation α on page 631 where he has already assumed the TE value for $\rho(0)$ [just above equation α]. He uses D instead of L_d for the diagonalized matrix, and $V = e^{Lt}$.

So now at least we know what Malcolm is doing here.

C. Details of the Calculation.

So now we want to solve $L\phi_n = d_n\phi_n$ for the matrix L shown page 630. We can write our TI SE as

$$(L - d_n 1)\phi_n = 0$$

C1. Compute the eigenvalues

We know that if $\det(L - d_n 1) \neq 0$, we can invert this equation and we get $\phi_n = 0$ meaning there is no non-zero solution to the problem. We are looking for interesting solutions, so we require that $\det(L - d_n 1) = 0$, which is the secular or characteristic equation I suppose. [I am not powering up my ODE module at this time because that will cost several hours of swap time.] Setting $\det(L - d_n 1) = 0$ tells us what the eigenvalues are for our problem. We get

$$\begin{vmatrix} i\Omega_A - \lambda - k - d & k \\ k & i\Omega_B - \lambda - k - d \end{vmatrix} = 0$$

But to solve this mess, let $a = i\Omega_A - \lambda - k$ and $b = i\Omega_B - \lambda - k$ so we then have

$$\begin{vmatrix} a-d & k \\ k & b-d \end{vmatrix} = 0$$

Here are some algebra steps following the above:

$$(a-d)(b-d) - k^2 = 0$$

$$d^2 - (a+b)d + (ab-k^2) = 0$$

$$A = 1 \qquad B = -(a+b) \qquad C = (ab-k^2)$$

$B^2 - 4AC = (a+b)^2 - 4(ab-k^2) = (a-b)^2 + 4k^2 = 4 * \{ [(a-b)/2]^2 + k^2 \}$

But $(a-b)/2 = i(\Omega_A - \Omega_B)/2 \equiv i\Omega_\Delta/2$ so $[(a-b)/2]^2 = -(\Omega_\Delta/2)^2$ and we have

$B^2 - 4AC = 4 * \{ -(\Omega_\Delta/2)^2 + k^2 \} = -4 \{ (\Omega_\Delta/2)^2 - k^2 \}$

Then $\sqrt{B^2 - 4AC} = 2i\,R$ where $R = \sqrt{(\Omega_\Delta/2)^2 - k^2}$

Our solution is then, from the usual quadratic formula,

$d = (a+b)/2 \pm iR = i\Omega_{av} - \lambda - k \pm iR$ $\Omega_{av} = (\Omega_A + \Omega_B)/2$

This agrees with the bottom line on page 630, except Malcolm has omitted the $i\Omega_{av}$ term from his eigenvalues. Let's now define our d_1 and d_2 as Malcolm does apart from this factor

$d_1 = i\Omega_{av} - \lambda - k - iR \equiv d_-$

$d_2 = i\Omega_{av} - \lambda - k + iR \equiv d_+$ $d_\pm = i\Omega_{av} - \lambda - k \pm iR$

C2. Compute the eigenvectors and the matrix X

Now, how to we find the eigenvectors? In general, given equation Ax=0, how to you find the eigenvectors which span the 2D nullspace of A? It's easy: Imagine that $\phi = (u, v)$ column vector. Then we have

$$\begin{pmatrix} a-d & k \\ k & b-d \end{pmatrix}\begin{pmatrix} u \\ v \end{pmatrix} = 0 \quad \Rightarrow (a-d)u + kv = 0 \quad \text{and} \quad ku + (b-d)v = 0$$

The second equation says $ku = (d-b)v$. So set $v = 2k$ arbitrarily and get $u = (d-b)/k * 2k = 2(d-b)$. So our eigenvectors are therefore

$$\begin{pmatrix} u \\ v \end{pmatrix} = \begin{pmatrix} 2(d-b) \\ 2k \end{pmatrix}$$

Meanwhile, $2(d-b) = 2(i\Omega_{av} - \lambda - k \pm iR - [i\Omega_B - \lambda - k]) = 2(i\Omega_{av} - \lambda - k \pm iR - i\Omega_B + \lambda + k])$

$= 2(i\Omega_{av} - i\Omega_B \pm iR) = 2i\,(\Omega_{av} - \Omega_B) \pm 2iR$

but $2(\Omega_{av} - \Omega_B) = (2\Omega_{av} - 2\Omega_B) = (\Omega_A + \Omega_B - 2\Omega_B) = (\Omega_A - \Omega_B) = \Omega_\Delta$

so that $2(d-b) = i\Omega_\Delta \pm 2iR$ and our eigenvectors are therefore

$$\begin{pmatrix} u \\ v \end{pmatrix} = \begin{pmatrix} i\Omega_\Delta \pm 2iR \\ 2k \end{pmatrix}$$ // these are for eigenvalues $d_\pm$ respectively

This disagrees with Levitt equation α page 630 by a sign on the $i\Omega_\Delta$ term.

So, assuming my result is correct, I get the matrix X whose columns are eigenvectors

$$X = \begin{pmatrix} i\Omega_\Delta - 2iR & i\Omega_\Delta + 2iR \\ 2k & 2k \end{pmatrix} = \begin{pmatrix} i(\Omega_\Delta - 2R) & i(\Omega_\Delta + 2R) \\ 2k & 2k \end{pmatrix} \qquad = \{ d_- , d_+\} = \{d_1, d_2\}$$

C3. Compute X^{-1}.

I can look up the inverse of this on my "summary of matrix facts" page

$$X = \begin{pmatrix} a & b \\ c & d \end{pmatrix} \qquad \Rightarrow \qquad X^{-1} = \begin{pmatrix} d & -b \\ -c & a \end{pmatrix} / \det X$$

In our case $\det X = 2ki\,[\,(\Omega_\Delta - 2R) - (\Omega_\Delta + 2R)] = 2ki\,(-4R) = -8kiR$. We then get

$$X^{-1} = \begin{pmatrix} 2k & -i(\Omega_\Delta + 2R) \\ -2k & i(\Omega_\Delta - 2R) \end{pmatrix} / (-8kiR) = i \begin{pmatrix} 2k & -i(\Omega_\Delta + 2R) \\ -2k & i(\Omega_\Delta - 2R) \end{pmatrix} / (8kR)$$

$$= \begin{pmatrix} 2ik & +(\Omega_\Delta + 2R) \\ -2ik & -(\Omega_\Delta - 2R) \end{pmatrix} / (8kR) = \begin{pmatrix} 2ik & 2R + \Omega_\Delta \\ -2ik & 2R - \Omega_\Delta \end{pmatrix} / (8kR) = X^{-1}$$

Again we agree exactly except for the sign of Ω_Δ, see his α' on page 630.

C4. Compute ρ(t) assuming that ρ(0) = (1,1).

Now finally let's compute α on page 631 as follows

$$X^{-1} \begin{pmatrix} 1 \\ 1 \end{pmatrix} = \begin{pmatrix} 2ik & 2R + \Omega_\Delta \\ -2ik & 2R - \Omega_\Delta \end{pmatrix} / (8kR) = (1/8kR) \begin{pmatrix} 2ik & 2R + \Omega_\Delta \\ -2ik & 2R - \Omega_\Delta \end{pmatrix} \begin{pmatrix} 1 \\ 1 \end{pmatrix} =$$

$$= (1/8kR) \begin{pmatrix} 2ik + 2R + \Omega_\Delta \\ -2ik + 2R - \Omega_\Delta \end{pmatrix}$$

Since the eigenvectors were put in 1,2 order within X (as shown above), our next operation is this:

$$\begin{pmatrix} e^{d1t} & 0 \\ 0 & e^{d2t} \end{pmatrix} X^{-1} \begin{pmatrix} 1 \\ 1 \end{pmatrix} = (1/8kR) \begin{pmatrix} e^{d1t} & 0 \\ 0 & e^{d2t} \end{pmatrix} \begin{pmatrix} 2ik + 2R + \Omega_\Delta \\ -2ik + 2R - \Omega_\Delta \end{pmatrix} =$$

$$= (1/8kR) \begin{pmatrix} e^{d1t}\,(2ik + 2R + \Omega_\Delta) \\ e^{d2t}\,(-2ik + 2R - \Omega_\Delta) \end{pmatrix}$$

The next step is to apply X to this result,

$$X\begin{pmatrix} e^{d1t} & 0 \\ 0 & e^{d2t} \end{pmatrix} X^{-1}\begin{pmatrix} 1 \\ 1 \end{pmatrix} = X\ (1/8kR)\begin{pmatrix} e^{d1t}(2ik + 2R + \Omega_\Delta) \\ e^{d2t}(-2ik + 2R - \Omega_\Delta) \end{pmatrix}$$

$$= (1/8kR)\begin{pmatrix} i(\Omega_\Delta - 2R) & i(\Omega_\Delta + 2R) \\ 2k & 2k \end{pmatrix}\begin{pmatrix} e^{d1t}(2ik + 2R + \Omega_\Delta) \\ e^{d2t}(-2ik + 2R - \Omega_\Delta) \end{pmatrix}$$

$$= (1/8kR)\begin{pmatrix} i(\Omega_\Delta - 2R)\, e^{d1t}(2ik + 2R + \Omega_\Delta) + i(\Omega_\Delta + 2R)\, e^{d2t}(-2ik + 2R - \Omega_\Delta) \\ 2k\ \ e^{d1t}(2ik + 2R + \Omega_\Delta) + 2k\ \ e^{d2t}(-2ik + 2R - \Omega_\Delta) \end{pmatrix}$$

and if we add (1/2i) from TE [his assumption page 631] we get our final result which is this:

$$\rho_-(t) = (1/2i8kR)\begin{pmatrix} i(\Omega_\Delta - 2R)\, e^{d1t}(2ik + 2R + \Omega_\Delta) + i(\Omega_\Delta + 2R)\, e^{d2t}(-2ik + 2R - \Omega_\Delta) \\ 2k\ \ e^{d1t}(2ik + 2R + \Omega_\Delta) + 2k\ \ e^{d2t}(-2ik + 2R - \Omega_\Delta) \end{pmatrix}$$

Now we know that we simply add the two ρ_- contributions (that is $\rho_{A-} + \rho_{B-}$) to get our total NMR signal, so we then get

$$\rho_{NMR}(t) = (1/2i8kR)\ [i(\Omega_\Delta - 2R - 2ik)\, e^{d1t}(2ik + 2R + \Omega_\Delta) + i(\Omega_\Delta + 2R - 2ik)\, e^{d2t}(-2ik + 2R - \Omega_\Delta)\ ]$$

Take a common i out and cancel it, and reorder some terms to get

$$\rho_{NMR}(t) = (1/16kR)\ [(\Omega_\Delta - 2R - 2ik)\, e^{d1t}(2ik + 2R + \Omega_\Delta) + (\Omega_\Delta + 2R - 2ik)\, e^{d2t}(-2ik + 2R - \Omega_\Delta)\ ]$$

$$= [\ K_1\, e^{d1t} + K_2\, e^{d2t}]\ /16kR$$

where

$$K_1 = (\Omega_\Delta - 2R - 2ik)(2ik + 2R + \Omega_\Delta) = [\ \Omega_\Delta - 2(R+ik)\ ][\ \Omega_\Delta + 2(R+ik)\ ]$$

$$K_2 = (\Omega_\Delta + 2R - 2ik)(-2ik + 2R - \Omega_\Delta) = -(\Omega_\Delta + 2R - 2ik)(+2ik - 2R + \Omega_\Delta)$$

$$= -[\ \Omega_\Delta + 2(R - ik)\ ][\ \Omega_\Delta - 2(R - ik)\ ]$$

So let's now summarize our final result

$$\rho_{NMR}(t) = [\ K_1\, e^{d1t} + K_2\, e^{d2t}]\ /16kR \quad \text{where}$$

$$K_1 = [\ \Omega_\Delta - 2(R+ik)\ ][\ \Omega_\Delta + 2(R+ik)\ ] = 8k(k - iR)$$
$$K_2 = -[\ \Omega_\Delta + 2(R-ik)\ ][\ \Omega_\Delta - 2(R-ik)\ ] = 8k(k + iR)$$

where the simpler forms arise from using $R^2 = (\Omega_\Delta/2)^2 - k^2$. Our result is now

$$\rho_{NMR}(t) = \{\ 8k(k-iR)/16kR\ \}\ e^{d1t} + \{\ 8k(k+iR)/16kR\ \}\ e^{d2t}$$

$$= \{(k-iR)/2R\}\ e^{d1t} + \{(k+iR)/2R\}\ e^{d2t}$$

$$= (-i/2)\ (\ 1 + ik/R)\ e^{d1t} + (-i/2)\ (\ 1 - ik/R)\ e^{d2t}$$

Now I think we are supposed to do this: (as for example on page 308 where s = a)

$$s(t) = 2i\ \rho_{NMR}(t) = (\ 1 + ik/R)\ e^{d1t} + (\ 1 - ik/R)\ e^{d2t}$$

and then my result agrees with Malcolm's γ on page 631 but I am missing a factor of 1/2. Otherwise everything is perfectly in agreement and I have incorporated his assumption for ρ(0).

Are we supposed to add the signals, or average them? Maybe that has something to do with the factor of 2.

What about his errata?

Page 630: The factor **Omega^bar** (defined in the first part of Eq.15.5) should be added to the values of both eigenvalues, defined in the last equation on the page.

Page 631: In the right-hand side of the third equation, replace 1/(2i) by **1/(4i)**. The factor of (1/2) arises since the initial spin order is divided between sites in the A and B states (see the first equation on page 628). The right-hand sides of the two following equations should also be divided by two. The last equation on page 631 is correct as stated.

OK, so he has already found both the errata I noted. If I assume that ρ(0) = 1/4i then I will get that extra factor of 1/2 on the last equation, so I then agree with his equation γ. The 1/4i agrees with top of page 308 if you set Boltzmann B = 1 which seems a good way to fly. Whatever the correct logic is, I am happy with my result here.

But, it is really $i\Omega_{av}$ we want to add, so I have another errata to report. So I will report two problems for this section.

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17.12.4 Longitudinal magnetization exchange. Holding off on this till I need it. // I need it now! Let's write out one of the implied equations here:

$$d\rho_{A\alpha} = (-W-k)\ \rho_{A\alpha} + W\ \rho_{A\beta} + k\ \rho_{B\alpha} + 0\ \rho_{B\beta}$$

Here, W is the β→α "transition rate" (probably for either the A or B species). This is caused by T_1 type relaxation processes. Here we see +W for incoming, and -W for outgoing, seems OK. Meanwhile, we have "exchange incoming" from $\rho_{B\alpha}$ and corresponding outflow from $\rho_{A\alpha}$ in the first term. The last term is 0 because you would have to have something like W*k to make it go into the left hand side. Lets now write the other three equations based just on the above (don't look at the matrix yet):

$$d\rho_{A\beta} = W\,\rho_{A\alpha} + (-W-k)\,\rho_{A\beta} + 0\,\rho_{B\alpha} + k\,\rho_{B\beta}$$

This was equation #2 and we swapped the first pair and the last pair. Agrees with matrix. Next

$$d\rho_{B\alpha} = k\,\rho_{A\alpha} + 0\,\rho_{A\beta} + (-W-k)\,\rho_{B\alpha} + W\,\rho_{B\beta}$$

I did this one by hand, and it agrees with row 3 of the matrix. Finally

$$d\rho_{B\beta} = 0\,\rho_{A\alpha} + k\,\rho_{A\beta} + W\,\rho_{B\alpha} + (-W-k)\,\rho_{B\beta}$$

So, I now agree with the form of L_{pop}.

Now let's derive (17.79) using the above:

$$dI_{Az} = d\rho_{A\alpha} - d\rho_{A\beta}$$
$$= [\,(-W-k)\,\rho_{A\alpha} + W\,\rho_{A\beta} + k\,\rho_{B\alpha} + 0\,\rho_{B\beta}\,] - [\,W\,\rho_{A\alpha} + (-W-k)\,\rho_{A\beta} + 0\,\rho_{B\alpha} + k\,\rho_{B\beta}]$$

$$= (-2W-k)\,\rho_{A\alpha} + (2W+k)\,\rho_{A\beta} + k\,\rho_{B\alpha} - k\,\rho_{B\beta}$$

$$= (-2W-k)[\,\rho_{A\alpha} - \rho_{A\beta}] + k\,[\rho_{B\alpha} - \rho_{B\beta}]$$

$$= (-2W-k)\,dI_{Az} + k\,dI_{Bz} \qquad \text{// which is the top row in the 17.79}$$

The lower row is symmetric so I agree now with (17.79).

Now we are back to our old problem which we treated above

$$L\phi_n = d_n\phi_n \qquad L\rho = d\rho/dt \qquad \rho(t) = e^{Lt}\,\rho(0)$$

except we replace $\rho \rightarrow (I_{zA}, I_{zB})$. But let's just keep the notation exactly as it was and grind the gears again:

C1'. Compute the eigenvalues

As we did above, we set det (L-d1) = 0. We have exactly the same form we had last time, except now we have a = b = -2W-k. Here are the calculations we did last time maintaining $a \neq b$:

$$\begin{vmatrix} a-d & k \\ k & b-d \end{vmatrix} = 0$$

Here are some algebra steps following the above:

$$(a-d)(b-d) - k^2 = 0$$

$$d^2 - (a+b)d + (ab-k^2) = 0$$

$A = 1 \qquad B = -(a+b) \qquad C = (ab-k^2)$

$B^2-4AC = (a+b)^2 - 4(ab-k^2) = (a-b)^2 + 4k^2 = 4 * \{ [(a-b)/2]^2 + k^2 \}$

Now setting a = b we have $B^2-4AC = 4k^2$ so our quadratic formula eigenvalues are

$d = (+2a \pm 2k)/2 = a \pm k = (-2W-k) \pm k = -2W - k \pm k$

$d_+ = -2W \qquad = d_2$
$d_- = -2W - 2k \qquad = d_1$

which agrees with Malcolm bottom of page 632. Note that $(d_\pm - a) = \pm k$.

C2'. Compute the eigenvectors and the matrix X

We first steal our result from last time, setting b = a to get

$$\begin{pmatrix} u \\ v \end{pmatrix} = \begin{pmatrix} 2(d-a) \\ 2k \end{pmatrix}$$

But the numerator is then either +2k or -2k, so the eigenvectors are (1,1) for $d_+ = d_2$ and (-1,1) for the other one. Putting d_1's column vector first, we get exactly the X matrix Malcolm shows.

C3'. Compute X^{-1}.

I can look up the inverse of this on my "summary of matrix facts" page

$$M = \begin{pmatrix} a & b \\ c & d \end{pmatrix} \qquad \Rightarrow \qquad M^{-1} = \begin{pmatrix} d & -b \\ -c & a \end{pmatrix} / \det M$$

so here we go:

$$X = \begin{pmatrix} -1 & 1 \\ 1 & 1 \end{pmatrix} \qquad \Rightarrow \qquad X^{-1} = \begin{pmatrix} 1 & -1 \\ -1 & -1 \end{pmatrix} /(-2) = (1/2) \begin{pmatrix} -1 & 1 \\ 1 & 1 \end{pmatrix}$$

in agreement with Malcolm.

C4'. Compute ρ(t) assuming that ρ(0) = (1,0).

Recall our task at hand. Our variables are really $\rho = (M_{Az}, M_{Bz})$, the z-directed magnetizations for A and B spin species. We could start in a situation where only A is polarized and B is not, call that the (1,0) situation [which we can scale later]. If we find that $\rho(t) = (a,b)$ at some later time, then we can say to ourselves that the polarization of the A species somehow spread (transferred) into the B species in amount b, and stayed in the A species in the amount a.

So we do our calculation of the final ρ in the usual steps, copying from above:

$$X^{-1}\begin{pmatrix}1\\0\end{pmatrix} = (1/2)\begin{pmatrix}-1 & 1\\ 1 & 1\end{pmatrix}\begin{pmatrix}1\\0\end{pmatrix} = (1/2)\begin{pmatrix}-1\\1\end{pmatrix}$$

$$\rightarrow \begin{pmatrix}e^{d1t} & 0\\ 0 & e^{d2t}\end{pmatrix}(1/2)\begin{pmatrix}-1\\1\end{pmatrix} = (1/2)\begin{pmatrix}-e^{d1t}\\ e^{d2t}\end{pmatrix}$$

$$\rightarrow \begin{pmatrix}-1 & 1\\ 1 & 1\end{pmatrix}(1/2)\begin{pmatrix}-e^{d1t}\\ e^{d2t}\end{pmatrix} = (1/2)\begin{pmatrix}e^{d1t}+e^{d2t}\\ -e^{d1t}+e^{d2t}\end{pmatrix}$$

So the amount staying in A is the top line

$$A\rightarrow A = (1/2)\left[e^{d1t}+e^{d2t}\right] = \left[e^{-(2W+2k)t}+e^{-2Wt}\right]/2$$

$$= e^{-2Wt}\left[e^{-2kt}+1\right]/2 = e^{-2Wt}e^{-kt}\left[e^{-kt}+e^{+kt}\right]/2$$

$$= e^{-(2W+k)t}\cosh(kt)$$

At this point, it is claimed that the transition rate W implies $T_1 = 1/(2W)$ [maybe next chapter for the constant], so we then have

$$A\rightarrow A = \cosh(kt)\exp\left[-(k+T_1^{-1})t\right]$$

If we compute the amount into (0,1) which ends up as all B mag, we get minus sign on the e^{d1t} term which then makes the same result but sinh,

$$A\rightarrow B = \sinh(kt)\exp\left[-(k+T_1^{-1})t\right]$$

Now I need some words about what in fact we just did here as it relates to the pulse sequence because it is very hazy right now. On page 506 we see some "density matrix" entering the mixing pulse at time 4. We have thrown out I_T terms due to our phase cycle filter.

What exactly is the item A→A above? IO can see that this item has a value real and ≤ 1 from an earlier form above $e^{-2Wt}\left[e^{-2kt}+1\right]/2$. I think it is a probability. What does M_{Az} mean, an element of our 2-vector? It is the +z directed polarization carried by the A spin species. So A→A = .7 would mean that 30% of the zmag of A went over to the B guys, apart from the T_1 loss. Notice this fact:

$$A\rightarrow A + A\rightarrow B = e^{-2Wt}\left[e^{-2kt}+1\right]/2 + e^{-2Wt}\left[-e^{-2kt}+1\right]/2 = e^{-2Wt} = e^{-t/T1}$$

OK, so these are probabilities that the $zmag_A$ stays on A or moves over to B.

Back to the inline chapter 15 notes now.