This document covers two sequential appendices.

Appendix 17.13 The Solomon Equations 3.27.08

The idea here is very simple. We have our usual four populations for a 2-spin system. Because of the non-zero transition probabilities W_i, probability is constantly leaking between the four states in a controlled way, and this provides "relaxation" toward equilibrium. Our first problem here was to verify the matrix at the bottom of page 33 which describes these ebbs and flows. The first row of the matrix corresponds directly to the equation top of page 534. I wrote down all four of the equations by staring at pages 528 and 529. Each of the four states has three outbound leakages (each proportional to the population of the starting state), and three inbound leakages from the other three states. You use the arrows in the two pictures for the rates. For example, inbound to $\rho_{\alpha\beta}$ from $\rho_{\beta\beta}$ is $[\rho_{\beta\beta} * W_{+\beta}]$. It is always proportional to the source population. Although very tedious, I was able to verify that the matrix bottom of page 633 is exactly correct, all 16 elements are right. Notice that all four equations are then contained in the one vector equation $dP/dt = W_P P$, the first of which appeared on page 524.

The next problem was explaining the line Z = TP on page 634. Here is a sample calculation:

$$\begin{aligned} \langle 2I_{1z}I_{2z}\rangle &= \rho_{\alpha\alpha}\langle\alpha\alpha|\, 2I_{1z}I_{2z} \,|\alpha\alpha\rangle + \rho_{\alpha\beta}\langle\alpha\beta|\, 2I_{1z}I_{2z} \,|\alpha\beta\rangle \\ &\quad + \rho_{\beta\alpha}\langle\beta\alpha|\, 2I_{1z}I_{2z} \,|\beta\alpha\rangle + \rho_{\alpha\alpha}\langle\beta\beta|\, 2I_{1z}I_{2z} \,|\beta\beta\rangle \\ &= 2*1/2*1/2\ \rho_{\alpha\alpha} + 2*1/2*(-1/2)\ \rho_{\alpha\beta} + 2*(-1/2)*1/2\ \rho_{\beta\alpha} + 2*(-1/2)*(-1/2)\ \rho_{\beta\beta} \\ &= (1/2)\,[\ \rho_{\alpha\alpha} - \rho_{\alpha\beta} - \rho_{\beta\alpha} + \rho_{\beta\beta}\ ] \end{aligned}$$

and this gives the last row of the T matrix.

Next, how do we know that this matrix is its own inverse? Not obvious staring at it. I typed it into Maple and had Maple compute the inverse.

```
U := (1/2)*matrix (4,4,[1,1,1,1,1,1,-1,-1,1,-1,1,-1,1,-1,-1,1]);
inverse(U);
```

Thus, $T^{-1} = T$ and $T^2 = 1$. This is a property of a matrix which is symmetric and orthogonal. I think I know it is orthogonal because the columns are independent (so it is unitary). So $T^\dagger = T^{-1}$ and $T = T^T$ and T = real, so $T = T^{-1}$, fine,

Now here is a derivation of (17.83):

$dP/dt = W_P P$ but $P = TZ$ so $TdZ/dt = W_P P$ so $dZ/dt = TW_P TZ = W_Z Z$.

I then had Maple compute the matrix 17.82 and it found the error noted in the errata. I saved the Maple code in this directory, here is the best I could make Maple produce:

$$\begin{bmatrix} 0 & 0 & 0 & 0 \\ W1\,B + W2\,B & -2\,W1 - W2 - W0 & -W2 + W0 & W2\,B \\ W1\,B + W2\,B & -W2 + W0 & -2\,W1 - W2 - W0 & W2\,B \\ 0 & W1\,B & W1\,B & -4\,W1 \end{bmatrix}$$

which agrees with 17.82.

Next, we know that the vector (17.84) is what we expect for TE. The 1 must be a 1, we expect no double correlation for the bottom component, and the middle two are :

$$\langle I_z \rangle = \mathrm{tr}(\rho I_z) = \mathrm{tr}([1/2 + B/2\ I_z]\ I_z) = (B/2)\ \mathrm{tr}(I_z^2) = (B/2)*1/4\ \mathrm{tr}(1) = (B/2)*(1/2) = B/4$$

I have carefully calculated this in the 2-spin system using page 365 and I still get B/4, not B/2, so I think I have found another errata. If I install (1,B/4,B/4,0) as Zeq, I find that $W_z Z_{eq}$ is equal to this:

$$\begin{bmatrix} 0 \\ \frac{1}{2}W1\,B + \frac{1}{2}W2\,B \\ \frac{1}{2}W1\,B + \frac{1}{2}W2\,B \\ \frac{1}{2}W1\,B^2 \end{bmatrix}$$ with B/4's

$$\begin{bmatrix} 0 \\ 0 \\ 0 \\ W1\,B^2 \end{bmatrix}$$ with B/2's

which is (0,0,0,0) in zeroth order in B, not first order as he claims.

Regardless, if we put in my Z_{eq} with the B/4 guys, (17.85) is still true because we are just subtracting two equations.

Now, it is true that he can *define* the vector Z_{eq} as shown, and it is true that the equations will imply that $dZ_{eq}/dt = 0$ which would seem to be what we mean by equilibrium. Still, something is fishy here!

Moreover, right on page 524 he states clearly that $\langle I_{1z} \rangle^{eq} = B/4$! We know that we have made small-B approximations in various places, so maybe it is just coming home to roost here.

Now moving to page 635: Equation (17.85) is valid as long as Z_{eq} satisfies Z' = WZ, but true, we expect this to be zero for "eq". I don't have a problem with this equation.

Next he throws all linear B terms out of (17.82) and that does give the second equation on page 635, with the correction in the lower right corner which maintains block form. It is then trivial to show the final results.

Solomon Equations: These are controlling the $\langle I_{1z} \rangle$ and $\langle I_{2z} \rangle$ as functions of distance each is away from EQ. The matrix elements are as shown and are thus functions of the three rates. I could do these

linear combinations to get the net results. These equations are telling us what happens to the individual longitudinal spins as a function of time due to the various transition rates W_i. I would think the factor of π would be important here, it would scale up the entire matrix by π. I will pay attention to this issue when I get back to the main line text.

Appendix 17.14 Cross-Relaxation Dynamics 3.27.08

Now suppose we throw out the EQ values of $\langle I_{1z} \rangle$ and $\langle I_{2z} \rangle$, pretending B = 0 since B << 1. We get the equation shown and I agree completely with (17.86) which just converts the solution to a previous exchange problem to be the solution of our current problem. I definitely think my π factor affects these solutions because if scales things like R_{auto}. The 2x2 equation solutions here are used in the NOESY pulse sequence analysis, and the "traverse version" of these same equations are used for ROESY,