Appendix 17.9 about Spin Echo Sandwiches

We start out with our standard full form for the J-coupled spin system and write the sandwich formula down. Then we look at two special cases, each of which produces a result of similar form. In this section, we are just stating the results.

The "short duration" case requires that τ is smaller than something as shown in 17.29, and you get the standard converted form for the result (17.30) where after the π pulse, the system behaves as if free-propagating by what Malcolm calls H^{strong} which is the full dot product interaction term.

The "long duration" case requires that τ be larger that something as shown in 17.34, but we also are assuming the "weak coupling limit" as shown in 17.33 which let's us use the z-form of the dot products. This results in that same form but now instead of H^{strong} we have H^{weak} which is JUST the s-form reduced dot product term.

17.9.1 Derivation of the short duration limit (595). The first step is to convert the sammy propagator U_{SES} to the form shown mid page 596. The only interesting item used here is that $R_x(\pi)$ negates I_z which seems pretty obvious. This then negates the non-J coupling term only, and then later when this is added to the original Ham, this term gets cancelled out, which is the whole point of doing the π pulse. The final trick of this section is to say that when τ is small, you can say $e^{\tau A}\, e^{\tau B} = e^{\tau(A+B)}$ and then we get the final result shown in (17.36), QED.

17.9.2 Derivation of the long duration limit (596). We start with the same general intermediate result derived in the last section, which here is numbered 17.37. We put in the z-forms of the dot product spins based on the usual "weak coupling secular" situation and the result falls out as before without any expo approximations. But a hidden assumption here is that the propagation times $\tau/2$ have to be long enough that you are allowed to use the secular weak coupling approximation, which means I think that there is time for the non-z terms to dephase so they are dephased during most of the pulse. The final result is 17.40, which is exactly as advertised.

It is in this section that Levitt claims that $R_x(\pi)$ commutes with "z spins" so you could in this case at least *think of* the π pulse before or after your τ free propagation. This is the theorem I proved above, that $[R_x(\pi), I_{1z}\, I_{2z}] = 0$. I think this is very non-obvious and Levitt is sneaking it in without comment.

I think this same "think of π as before or after the τ period" also applies in the general and the strong case, because $[R_x(\pi), \sigma_j] = 0$ so $R_x(\pi)$ commutes with any spin combination.

17.9.3 Hungry? Why not have several sandwiches. (597). It is pretty trivial to compute the "equivalent J-coupling-only" propagator for a number n of sequential sandwiches. Result is 17.41 and 42, and here he is admitting that $R_x(\pi)$ slides through either Hamiltonian J part, weak or strong. The phase of $R_x(\pi)$ will be $(-1)^N$ where N is the number of spins in your system. For the AX system of Chap 12, we have N=2 so $R_x(\pi) = 1$ and there is no phase for any number of sandwich pulses. The net result is that you create an effective J-only propagation period of $n\tau$ when you do n of these SES sequences.

17.9.4 Heteronuclear SES. This case is always in the weak coupling, long duration limit. However, to get the same conclusion, you have to arrange for simultaneous π pulses for the two species which Malcolm likes to call I and S. Remember that a "π pulse" is a duration such that $\beta t = \pi$, but now our two species have different betas. Also, the frequency of the π pulse RF is supposed to be at resonance, but

now we have two different resonances. So you really would need two RF pulse generators to do this combined experiment, the two pulses are at different Larmor frequencies and have different time durations, though this little detail does not show in the page 599 picture. The result of doing all this work is that the entire I + S system then runs effectively with only J couplings and "no chemical shifts". This last must then mean that you won't get spectral lines at the usual chem shift locations because your SES has removed that energy.

Now suppose you only apply a mid π pulse to the I species and not the S species? Picture is then page 600, and claim is that only the I will have its chem shift suppressed. The S species will propagate in the normal manner as if there were no pulse applied at all. I did not check the final conclusions of this section, and will only if this is applied somewhere.

End of appendix 17.9 It was a good one.