---------- **Chapter 15: Motion (479-511) ------- 32 p ---------- ###** 3.25-26.08

15.1 Motional Processes (479)

15.1.1 Vibrations (479). If a sticking-out H vibrates back and forth ± 15 degrees, you get **libration** on order of psec.

15.1.2 Group rotations (480). CH_3 and NH_3 rotate around the connecting axis at psec rate, slower if there is hindrance.

15.1.3 Flexibility (480). As large pieces of a protein wiggle around, you can measure their motion. Plate two shows this flexibility or mobility by color, red parts flex the most. Timescale I presume would depend on the mass of the piece in question in usual HO manner.

15.1.4 Chemical Exchange (480). Suppose an H jumps back and forth as shown. The NMR spectrum will be different for the two positions, you can perhaps detect this activity. P 481 top shows two CH_3 groups in non-equivalent locations which can swap by rotation, and NMR can detect even this. Timescale here would depend on bond strength and so has a huge range of ns to sec. Claim that NMR can see stuff even if in equilibrium.

15.1.5 Rotations of entire molecule (481). We can see this due to its effect on averaging, as we saw many times in the Ham section of this book. Timescale from ps to ns. For large bio molecules, rule is that timescale is t (nsec) = (1/2) m (Daltons).

15.1.6 Rotation of a solid (482). Picture shows a solid NMR sample that is spun on its axis, which axis sits at the magic angle relative to B. This situation is called **MAS** (**Magic Angle Spinning**). The magic angle causes the d-d coupling to vanish, as I look back. Top page 483 shows the effect of MAS on the spectrum of a solid powder spun at 0, 1 and 12 kHz. The results are rather amazing I think.
[see **magic angle spinning.doc** notes. This is a subject not analyzed in this book.]

15.1.7 Translation (483). Recall diffusion and flow. Recall how **diffusion** averages short range spin interactions at the microscale. At the macroscale, you can track diffusion or flow with a gradient, so this would be DFI MRI, whatever the term is. Gradients are used a lot in NMR analysis to analyze diffusion and flow, but Malcolm won't do any examples, see his refs. Oil in rock, blood flow, etc.

15.2 Motion Timescales (485). The picture summarizes the ranges for the processes considered above. Then we have three general timescale markers shown. The longest is T_1 on the left, relaxation timescale. On the right is the time it takes for Larmor single rotation, The middle is the general width of a spectrum, meaning the width that chemical shifts typically causes. These scales are sec, μs and ns roughly.

15.3 Motional Effects (486). It motion is very fast, then you get to "average the Hamiltonian" before the secular approximation is made. If slower, then you average after secular approx. (middle item). Slower motion can affect line-width perhaps this is T_2. Very slow can maybe let you do Bloch equations in classical sense, I am just guessing. We are going to see examples of most of these cases.

15.4 Motional Averaging (487). Super fast motion, as noted above, means pre-average into the Ham. Claim is made that relaxation comes from non-secular terms, hold till next chapter ponder that. The NMR signal comes mainly from the secular terms. Example of the first: that fast libration of H in C-H affects the d-d coupling, changing the value of b from what you think it should be based on the known bond distance. Since this is a super fast, the right approach is to just adjust b. In terms of NMR spectra, you should average spin stuff if faster than the spectral time scale. I am not conformable with the picture shown on page 488, don't know what the exit arrows mean.

15.5 Motional Lineshapes and two-site Exchange (488). We set up the exchange process as in the Appendix and we look at two regimes on page 490 which are small k and large k, relative to the Ω_Δ.

15.5.1 Slow intermediate exchange and motional broadening (490). We are in the small k regime, so square wave A,B is slow compared to the frequency gap. As you increase k, the exchange acts to damp off the FID. To make curves like this, you have to simulate the A-B random jumps, and add up the waveforms.

Now finally we get to use our hard-earned Appendix 17.12 result from page 631. It is then pretty clear that for small k we have two peaks and they are at $\Omega_{av} \pm R$ and k adds to the inherent width which is not surprising. As k increases toward the critical value that makes R = 0, the two peaks gradually merge into one broad peak, as very well shown on page 493. As noted above, for k = 0 you expect two clean lines, and for large k, you expect things to be washed out.

I think they will claim that this analysis is only valid when k is smaller than the critical value, and for larger k, we need the next section.

15.5.2. Fast intermediate exchange and motional narrowing (493). The result here is at first very odd. Claim is that this central peak narrows as you continue to increase k, spectrum shown page 495. This result follows exactly from our appendix-derived results. In fact, start with 15.4 and make the replacement $R \rightarrow iR$ to get the result in the large k regime. This moves R from the frequency argument to the decay argument, and also as $k \rightarrow \infty$ we get $R \rightarrow k$. We get precisely the results stated in 15.6. Now both lines are at the average frequency, so you no longer get "two lines" at all. the second term vanishes in the large k limit due to the (1-k/R) factor, and what remains is the first term which we see has -R, so it gets narrower as k increases and eventually gets to the λ limit. In this regime switching is so fast that the system sees the average chemical shift for all values of k. So we got a lot of mileage out of our appendix! These are great results to understand, I would have never guessed.

Next, he puts the spectra shapes on the timescale picture page 495 bottom, which is very nice. So now we see why $\Omega_\Delta/2$ is a point of significance in the spectrum world. Small k regime is to the left and you get two peaks, large to the right and you get a narrowing single peak.

Finally, we have some experimental NMR plots taken for a fixed material but varying T which we surely know will cause k to change due to the activation energy for the reaction. The expression shown for k(T) looks pretty obvious to me even knowing nothing about it. Gets the **Arrhenius** name on it, I think I have book derivations for this formula. The "material" is none other than the molecule shown on page 481 and we are looking at the ^{13}C spectra. The A and B refer to the two environments of this C spin. They had to "enrich" the gas to get a pair of ^{13}C's.

So as claimed, even though we are in an equilibrium situation with our exchange NMR sample, we are able to use NMR to measure k(T)!

15.5.3 Averaging of J-splittings (496). In the previous section, we had a physical exchange with rate k as something affecting time evolution of ρ. This k was causing spins to experience two different environments called A and B. The factor k appeared in the form $d\rho/dt = -k\rho + .. .$ If we think about an I and S hetero J coupled system, and we look at the spectrum for S, we can "think of" the T_1 relaxation processes acting on I as causing an "exchange" in the I system (swapping α and β for spin 1/2 I), and this "exchange" in the I system causes the S spin to see two different environments, so we can simply take over our results of the last section. We know that the appropriate k factor is going to be proportional to $1/T_1$ since this is how it appears for example in the Bloch Equations. The prop constant is 1/2, and maybe in the next chapter we will learn why. You really have to re-derive the starting system of equations to see how things will come out. We know that Ω_Δ for our J-coupled system will be $2\pi J_{IS}$ since that is the normal splitting in the absence of this "exchange effect".

So, assuming this is correct to do, when there is only small (slow) relaxation in the I system, we expect to see our line doublet in the S system. As the I system relaxation increases (T_1 gets smaller, faster)), our two lines are cut down and move together, and at a critical value we get a broad peak. Then as T_1 gets smaller still, we expect this peak to get narrower. This is shown page 497.

A comment says that this effect is often seen when I is an electric quad spin because T_1 is fast for such a spin, fast relaxation (next chapter). Of course in this case we need I > 1/2.

15.5.4 Asymmetric two-site exchange (497). Here you would have to redo all our equations but with k and k'. I guess in 17.76 you would have k' in two places, so matrix L would be different. I imagine that the exact same method would be carried out as in the appendix. Malcolm claims that k/k' is in fact exactly the K equilibrium constant we always use in chemistry which is also equal to the usual molarity ratio. So we expect to see K appear in the resulting spectral splitting and K=1 is the case we have already treated. This is true, and the result is shown on page 498: as you increase k, the peaks which were separate (and of unequal height because unequal TE concentrations) move together and merge into a single peak. Rather than being in the middle, this final peak is offset due to $K \neq 1$. This is crudely reasonable because the peak is offset toward the originally stronger peak as shown in the picture page 498. Fine, good to know, and have it so stated. You can thus use NMR to measure K for a reaction! We expect K to vary strongly with temperature.

Comment: I suppose that "even today", there is a lot to be learned about "molecules" in solution. You can't directly look at them very well, they are too small, and looking at them in action is what you might like to do, not when they are plastered up for a TEM shot. NMR gives a reading on live performance of a molecule, with suitable averaging. We might measure K, or bond lengths or angles, etc, using NMR.

15.5.5. Knight Shift (499). Mostly in this book we have dealt with interactions between two nuclear spins, such as the d-d through space, and the J-coupling through a bond. We have not talked much about the effect of electron spins on nuclear spins. Since the electron μ is 1000x larger than the nuclear one (see chap 1 notes), we might expect to see significant results. Electron pairing tends to remove such effects, and in most molecules you have such pairing, but I would guess not all. So I would expect to see some effect here in normal molecules.

This section, however, is about metals, not normal molecules. We know there are conduction electrons in the conduction band and these have spins, and they are unpaired, so we expect an effect.

Because μ is so large, there is a large energy difference [for a given B_0] between the α and β state for each electron, much *larger* in fact than kT, the opposite of what we are used to. So we now fit this physical situation into the context of our current discussion: Relaxation T_1 effects cause the *electron* spins to flip back and forth, causing an asymmetric exchange effect upon the nuclear spin. It is like you are measuring an S spin, and the electrons are the I spins which are relaxing. Since relaxation is fast in this metal case, you tend to be in the "single line" large k limit all the time. Because things are asymmetrical, we find that the single line is offset from the center of the two lines you would have at low k (in this case, high temperature). The offset from the center is called the Knight shift from our friendly UC Berkeley professor **Walter Knight** (who was there when I was there, but I never met since he was in a completely different field). He died in 2000 and found this shift around 1949, just after Purcell opened the NMR door. As you lower temperature, the α/β difference increases, asymmetry increases, the Knight shift increases. But when you set to spin-pairing in supercold, Knight reduces again since fewer unpaired electrons. I never studied BCS theory, another gaping hole in the history.

15.5.6. Paramagnetic shifts (500). Unpaired electrons in paramagnetic materials do the same thing as above. Paramagnetic means you have some fixed spins that can be lined up (perhaps spin and orbital). Diamagnetic is the induced-spins situation.

15.6 Longitudinal Magnetization Exchange (500). How could you measure k in a two-site exchange process when k is very small? It does affect the broadening of the narrow peaks, but that is hard to measure and is mixed up with λ. Here we learn of a pulse sequence which can bring out k !

15.6.1 The pulse sequence for "two-dimensional exchange spectroscopy". We see it here, where the FID and the first gap are the two time coordinates, and τ_m is held fixed for each 2D experiment. This is fancied up with the usual States mechanism using a phase cycle shown on page 502. In the "theory section" to follow, we shall learn that there are four peaks as shown on page 502, where the cross-peaks will be a measure of the presence of "k", the exchange rate. This method applies to any "exchange situation" characterized by some k, but perhaps think of the two CH_3 swapping groups we first studied.

The theory will say there are four peaks as shown, and the peak spectral amplitudes "a" will be given by the functions shown in 15.7. Note the first appearance of hyperbolic functions in this book! You can do your experiment at various τ_m values and make a fit to the ratio of the peak amplitudes that you get. The ratio of peak amplitudes is a $\tanh(k\tau_m)$ function, as plotted on page 504. So imagine running this experiment for a few τ_m values toward the left end. You then do a straight line fit and the slope will be $k\tau_m$ and bang, you have a value for k. This linear range of tanh they call the initial rate regime. All fine, we are now ready for the theory.

15.6.2 Theory for the above. We start off "working through" the pulse sequence to the start of the mixing period τ_m . We have (15.10) for the A species ρ, and similarly for the B.

A. Phase cycle and filter. Our first problem is to understand why the transverse parts are filtered away by the pulse sequence. First, recall the meaning of "order" of a coherence. The population coherences like $\rho_{\alpha\alpha}$ for a single spin-1/2 system have order = 0. These are the diagonal matrix element of ρ. If

you expand ρ in terms of spin matrices, we know that I_x and I_y are non-diagonal, and only 1 and I_z are diagonal. Therefore, if our phase cycle somehow achieves the coherence flow shown on page 501 during the τ_m period, we know that only I_z and 1 terms of ρ can be passed through that stage as a filter.

OK, the phase cycling diagram shown on page 502 is essentially the same as that shown on page 620 which was a nested gizmo. As in that example (DQF cosy), the short cycle of N=2 on the front end really does not "do anything" that I can tell, so the main act is the N=4 cycle on the back end at the ϕ_3 pulse. This phase cycle is making a filter so that the -1 output is fed only by 0 and ±4 inputs to the last pulse.

Question: "in theory", what could a pulse like the ϕ_2 pulse do to the order flow? Well, for a single spin-1/2 system, you can never have anything by order = 0, ±1. But I suppose we might apply this "method" to a system of two spin-1/2's that are J-coupled, and then you could talk about ±2 orders as well. In general, an arbitrary pulse will do full linkage of all possible inputs to all possible outputs. For a single spin-1/2, you feed in ±1 into the ϕ_2 pulse shown here on page 501, you might expect to get all three 0 ±1 outputs. In fact this is exactly the case according to (15.10) where we see all three in I_z and I_x. So, the back-end filter with N=4 is certainly going to remove the ±1 components. I think an N=2 filter would have done the trick as well, in this case (barring subtleties not mentioned).

So I now agree with equation α on page 506. We are filtering out the non-longitudinal terms, which is to say, we are filtering out the ±1 coherences and we get only populations coming through.

B. The exchange action during the mix period Our next step is to look at Appendix 17.12.4 which I skipped on my first pass through that appendix. So go there, and then come back here. // I am back and I have successfully derived the expressions for the value of $M_{Az}(\tau_m)$ and $M_{Bz}(\tau_m)$ at the end of the τ_m period given that we started all $M_{Az}(0)$ and $M_{Bz}(0) = 0$. There is some probability for the mag to stay with A, and some probability for it to transfer over to the B species spins.

Interpret now the first equation on page 507: the A species density matrix at the end of the mixing period has two terms which get added. The first term uses the coefficient shown mid page 506 as the scaled amount of $M_{Az}(0)$ we start with, and this is then reduced by the A→A factor. The second term represents a contribution to A mag from mag that *started* on B spins but transferred to A spins during the mix. So this amount is scaled by the lower coefficient on page 506. Everything is I_z here.

So I agree with the first two equations on page 507, second is symmetric copy of the first. The final pulse on page 501 just does the usual knockdown putting the z to -y, and this gives the next equation pair. Since we set B/2 = 0 (Boltzmann), we get the 1/2i factors in going to ρ_- as shown page 289, so happy now with those. Each of these two terms then makes a FID as shown. So if we add the FID of the A spins to the FID of the B spins, we get a+b and that is what we have at page bottom, where now it is broken out into four terms. We can now SEE what the **spectrum** must look like in the Ω_1, Ω_2 plane conjugate to t_1 and t_2. We can see that the A→A and the B→B terms are the **diagonal peaks** which have the cosh function which is 1 at k=0. The other two terms are the **cross-peaks** and they have sinh which = 0 when k=0. Thus, we have verified the claims made in the earlier section that the cross peaks increase from nothingness as k increases from 0. We also learn that diagonal peaks get weaker.

So look back now on page 503 at the two curves. Both diagonal and cross peak amplitudes decay in the long run because of the T_1 effect. Perhaps in the range 0 to 0.1 is where we examine things. We are interested in small k, after all.

Page 508 then quotes the results of the SIN States sequence, exactly the same with cos→sin. Thus when we add it all up with the States machinery (still on my whiteboard today, recorded somewhere), we get the nice peaks shown at the bottom of page 508.

Now finally we can look at the **experimental data** shown on page 509. The molecule of interest is in the class known as organometals. In this case, the fact that the molecule has two arbitrary metals called Me is not the main point. It is the metal ion Re which switches its position as shown to give us an exchange effect. Of course this exchange effect is going to act on ALL protons in this molecule. As an example, in the left picture we have a proton H_B which is called H_L in the right picture. In the 1D spectrum, we get a pair of unequal peaks (two peaks because k is small, unequal as on page 498 because we have different rates k and k', notice the 75% and 25% species indications in the inset. For this proton we see the four peaks as claimed, and for this τ_m the cross peaks are substantial.

As usual, the 2D spectroscopy pulls things apart so you can see them. All the "boxes" are quite apparent in the picture. Many peaks are split by other effects in the molecule, probably J-couplings.

Comment: During the mixing period τ_m, as we try to trace what happens to the density matrix, we are thinking about not just the usual "free propagation with T_1decay" but in fact that is replaced with the effects of exchange action happening during this period. This is a "new thing" that can happen during the gap between pulses that we never talked about before this chapter of the book. During the mixing period, we are seeing

Note added: Suppose there were no W decay. then we would get

$$A \to A \;\; = e^{-2Wt}\,[\, e^{-2kt} + 1\,]\,/2 \qquad \to\; [\, e^{-2kt} + 1\,]\,/2 \;\to 1/2 \text{ as } t\to\infty$$

$$A \to B \;\; = e^{-2Wt}\,[\, - e^{-2kt} + 1\,]\,/2 \qquad \to\; [\, - e^{-2kt} + 1\,]\,/2 \;\to 1/2 \text{ as } t\to\infty$$

Basically the exchange process acts like entropy, it spreads the spin which was originally on the A spins onto both spins species equally. This is what is meant by the picture on page 506. He did not appeal to the conservation of angular momentum under strong H in this section, but that would have predicted the same result since claim is that **J** is conserved in each direction separately.

Clearly this whole method only works if k is small enough that you get two separate peaks in the 1D spectrum, meaning $k < \Omega_A/2$

15.6.3 Motional Regimes (509). The picture shows the regime where our "exchange spectroscopy" is useful. We are in the distant double-line region of the timescale. Also, if T_1 is too fast, then you lose your signal and it does not work, so need $k < T_1^{-1}$ as another condition.