---------- **Chapter 8: NMR in Isotropic Liquids (223-237) -------- 14 p ---------- ###**

8.1 Molecular spin system (223). As noted above, for iso system if we ignore long inter, we get

chem shift = $-\gamma\ \delta_{iso}\ B^0\ I_z$,
dipole-dipole = 0, // I see from above, but not obvious to me
J coupling = $2\pi\ J_{12}\ \mathbf{I}_1 \bullet \mathbf{I}_2$ for same nuclei. // the simpler z form for weak coupling

which results in equation (8.2) as claimed. The set of spins in a single molecule is called a **spin system**. For a general molecule with four spins (non-equivalent, see later), we write out all terms of the H as shown in (8.3). There are 4 chem shift terms because each spin has its own chem shift, and there are 4*3/2 = 6 J coupling terms. This suggests the **graphical idea** shown in mid page 224: each spin gets a shape to denote its unique chemical shift (4 shapes), and each spin-pair gets a line (6 lines) to denote the J coupling interaction.

8.2 Spin ensemble. Just a thermal ensemble of molecules of the same type as shown.

8.3 Motionally suppressed J couplings (225) There are **two situations** of interest.

(1) In ethanol it is likely that the OH group jumps around on the molecule very fast, spending little time in any one location. So J couplings to it will be washed out. This idea is **fast chemical exchange**.

(2) If a nucleus has a strong **quadrupole moment**, because the internal E field rotates rapidly and interacts strongly with the nucleus, the spin of that nucleus is going to get strongly coupled to the thermal environment, which means its T_1 will be exceedingly small like 1 μsec. Since RF pulses are much longer than this, the result is that such spins don't show up in NMR because they are re-thermalized faster than they can get de-thermalized (aligned). Normally we think of idealized spins as on "perfect bearings" which don't care about what the electrons of the molecule are doing so the spin stays pointed in the same direction even as the molecules bang around. But we know the spins really do interact somehow with everything else, and this general process is called "relaxation" and this is where $T_1 < \infty$ comes from.

Examples are given of nuclei having large quad moments which relax fast in this way. On the other hand, if you have some symmetry such as in NH_4^+ which makes the E field tiny at the nucleus, then T_1 is long even if the nucleus has a large quad moment (which ^{14}N does).

Comment: Let's run through this one more time. Suppose a nucleus has an electric quadrupole interaction. Your main B field will still align the spin, and your RF π/2 pulse will still tip it down to the -y axis. But as soon as the (strong) RF pulse goes away, the large EQ interaction between the spin and the rotating molecule's electric field will cause the spin to be thermalized back to the TE situation with T_1 = 1 μs, so such a spin cannot radiate an NMR signal that you could see, the signal dies in 1 μs. In other words, such a spin relaxes so fast, you cannot see any signal from it.

8.4 Chemical equivalence. In the first example on page 226, there is a symmetry which makes the two H's and the two F's equivalent, so we then draw the symbol as shown, where now chem shifts are pairwise equal, and also the J couplings are equal as line types show. The implication of the symmetry is that the two spins so related see the "exact same" electron cloud distribution, so they have the same chemical shift. Of course the cloud could be mirror-reflected.

Second examples are benzene and water, very nice. The C and O atoms have no spin since due to the even-even rule of chapter 1 above. [In the benzene case, there seem to be two different kinds of couplings, the ones going all the way across are thin lines, other non-adjacents are thick lines.]

Third example is ethyl chloride shown end-on bottom page 227. The two near H's are equivalent, and $H_1 \sim H_2$ as well due to a mirror symmetry. The H_3 is not in an equivalence set since no symmetry. However, since the C-C bond can rotate freely, in a mixture all three H's on the far C will in fact be equivalent after all, and we get the diagram shown page 228 Fig 8.9. Good "teaching by example" of the author here, it is the best way.

Fourth example Fig 8.10 points out that the normal pair H ~ H situation is now broken because the three far groups are inequivalent and break the symmetry. As the far bond rotates, you get conformations that don't have the same energy, so C-C axis rotation does not make our two H's equivalent.

Fifth example page 229. Here, a mirror plane makes the H pair on the left same as on the right, but within each pair, chem shifts will be different, H's are not equivalent. I dimly remember all this stuff from ancient days.

8.5 Magnetic equivalence (229). If two spins are equivalent, they have the same chemical shifts. If they also have *fully* symmetrical J couplings to *all* other spins, then the spins are **magnetically equivalent**. This allows further simplification of the Hamiltonian, namely, that you can simply delete all dot product terms that involve spins in the same magnetic equivalence group. This non-obvious fact is demonstrated on page 583 in the appendix (App 17.6, see discussion a few paragraphs below). For the moment, let's assume this is true.

Notice that on page 226, Fig 8.4, the two H's are chemically equivalent (same chem shifts), but their couplings to all other spins are not the same -- the solid black line is different from the dotted black line. so these two H's are not "magnetically equivalent".

First example is that the graphic icon bottom of page 230. Here we have dotted lines from each H atom to all the other spins (ignore the H-H bond in this assessment). So this becomes the symbol shown top of page 231, we just don't draw the group-internal J coupling lines. This example has two magnetically equivalent groups. Second example is that Fig 8.9 loses its "vertical" internal lines -- the lines are the same because the far three H's can rotate, recall. Water and benzene lose ALL their internal lines!

[BUT, this seems wrong for benzene because on page 227 the lines from a given C to the three non-neighbors are not the same, one thin line and two thick lines. So this is really like Fig 8.4. So we have a mystery here. But here is a comment from the web that explains the mystery: "If all nuclei in a molecule are chemically equivalent (benzene) they must also be magnetically equivalent since there is no other, different, nucleus which would allow the distinction between the chemical and magnetic equivalence"] See comment added below on this subject.

At the bottom of p231, we have an example of where spins in each group are equivalent, but not magnetically so because the J couplings are different, and we cannot simplify and are stuck with as shown top p 232. So this is a physical example of our diagram 8.4 which is now repeated as 8.18.

Third example is one where things are mag equiv and we get as shown page 232.

Appendix 17.6 on page 583. (Proof of Mag Equivalence claim) This appendix considers a Hamiltonian with three pairs of J-couplings (three spins 1,2 and 3) where 1 and 2 are magnetically equivalent. This means for example that $J_{13} = J_{23}$ and that 1 and 2 are chemically equivalent. We are not here in the isotropic approximation (where we set these J's to 0). The Hamiltonian becomes as shown top page 584 and we partition the Hamiltonian into A + B as shown where B contains the $I_1 \bullet I_2$ term. We then show

that [A,B] = 0 and also [Q,B] = 0 where Q is (I think) any normal function of the spins such as the sum of their x components (see comment below). Then, based on a general theorem proven on page 583, we conclude that any observable Q (at least of the form we assume) cannot depend on term B, so therefore we are allowed to remove B from the Hamiltonian. In this case, that means we can throw out $\mathbf{I_1 \bullet I_2}$, the dot product between the two spins that we assumed were magnetically equivalent. This then means that in your little graphics you can erase coupling lines between pairs of mag equiv spins.

First, we get a general theorem which is full proven.

Theorem: if H = A+B *and* [A,B] = 0 *and* [Q,B] = 0 for some observable Q, then <Q> does not depend on B and you can just throw B away in your calculation. The proof is done in the Heisenberg picture and is completely trivial.

Next, we apply this theorem to a J-coupled spin system with a magnetic equivalence group, and things are not so obvious here. Our Hamiltonian of interest is (8.2) from page 223. This has the normal z terms and then a sum of I•I terms. Each of these terms was discussed page 213. The term started as (7.46) but then isotropic-ness forced the J matrix to be diagonal and this leads at once to (7.49) which is where we now are. This appendix considers three such terms in a Hamiltonian as shown near the top of page 584.

I don't really understand the little hint given, so I do my own proofs. We have to show that [A,B] = 0 and also that [B,Q] = 0. Here is what I think is a canonical case for the [A,B] = 0 system. I will use J,K,L to represent three spins (rather than I_1 I_2 and I_3). Then consider:

$$[\ (\mathbf{J} + \mathbf{K})\bullet\mathbf{L},\ \ \mathbf{J}\bullet\mathbf{K}\ ]$$

Whether we think of **L** as a true third spin or as some constant vector, the commutator is the same:

$$= \mathbf{L}\bullet\ [\ \mathbf{J} + \mathbf{K}, \mathbf{J}\bullet\mathbf{K}\ ]$$

If we take L = (0,0,1) constant vector, then we are including in our case $[\ J_3 + K_3, \mathbf{J}\bullet\mathbf{K}\ ]$ which is another term which shows up in thinking about [A,B]. If we can show the above is 0, we have really done the entire [A,B] = 0 proof.

First you can show that the following identity is true in about 4 seconds

$$[\ \mathbf{J}, \mathbf{J}\bullet\mathbf{K}] = ih\ \mathbf{K} \times \mathbf{J} \quad \text{where } \mathbf{J} = \text{ang mom operators} \quad \mathbf{K} = \text{any vector}$$

Therefore $[\ \mathbf{J} + \mathbf{K}, \mathbf{J}\bullet\mathbf{K}\ ] = ih\ \mathbf{K} \times \mathbf{J} + (\mathbf{J} \leftrightarrow \mathbf{K}) = ih\ \mathbf{K} \times \mathbf{J} + ih\ \mathbf{J} \times \mathbf{K} = 0$ QED.

Now, what about the [Q,B] = 0 part of our proof? That depends on what Q is I suppose. Need to show that

$$[\ Q\ ,\ \mathbf{J}\bullet\mathbf{K}\ ] = 0$$

The only observable that our author considers is of the form $Q = J_1 + K_1 + L_1$ but we have already shown $[\ Q\ ,\ \mathbf{J}\bullet\mathbf{K}\ ]$ is 0 in this case, so for these Q's I agree.

Comment added later: The observable we really care about is $\langle \mathbf{M}_T \rangle$ because when this is non-zero, it makes a FID. But of course (for a single molecule) $\mathbf{M}_T = \gamma_1 \mathbf{I}_{1T} + \gamma_2 \mathbf{I}_{2T} + \gamma_3 \mathbf{I}_{3T} = \gamma_1 \mathbf{J}_T + \gamma_2 \mathbf{K}_T + \gamma_3 \mathbf{L}_T$ where $\gamma_1 = \gamma(1+\delta_1)$. But if 1 and 2 are chemically equivalent, then $\gamma_1 = \gamma_2$ and then $\mathbf{M}_T = \gamma_1(\mathbf{J}_T+\mathbf{K}_T) + \gamma_3 \mathbf{L}_T$. This entire operator commutes with $\mathbf{J}\bullet\mathbf{K}$ so falls into the "Q class". Thus, if we are trying to compute an expectation value of this transverse magnetization operator in any state ψ, the answer won't depend on the $B = \mathbf{J}\bullet\mathbf{K}$ term in the Hamiltonian, so we might as well throw it out right at the start. This then is why, if two spins are magnetically equivalent, you can through out the $\mathbf{J}\bullet\mathbf{K}$ term in the Hamiltonian for these spins. This means we are throwing out the J couplings between such spins, and graphically we then delete the J coupling line in the drawing.

Here is another argument: we know that $\langle \mathbf{I}_T \rangle = \mathrm{tr}(\rho \mathbf{I}_T)$ is the thing that makes the FID, even if all the spins are different. This shows that we are interested in $Q = J_1 + K_1 + L_1$ just as the appendix says, and this is a "Q class" Q and so the theorem applies.

Next, what about the case of a larger set of spins? He does a case with 3 of 4 spins being in a group. But the proof is exactly the same if you just do it by terms. Pick a J,K pair and use our result above. So I think this is all OK and I could show it for the general case.

Comment added later: Suppose you have a 3 spins that are mag equivalent. This case includes the case we just described above with three spins J,K,L, so we know we can "throw out" the J•K term from H'. But we can cyclicize the argument and then throw out K•L and then L•J so now we have thrown out ALL the J couplings. This is why, in a molecule which has N spins that are chemically and magnetically equivalent, we can throw out ALL the J couplings! This applies to water and benzene as shown on page 231 second figure up.

8.6 Weak coupling (233) If the chemical shifts of two spins are far apart compared to their J couplings, as measured by condition 8.8, then you can drop the corresponding spin dot product "off-diagonal" terms and you get the usual z-form shown in 8.9. That is, dot products are replaced with just their z term. So 8.7 would become 8.10. A good physical argument is given here as well: if two spins are Larmoring at much different frequency, their transverse component interactions are going to wash out. Just visualize those two spins spinning. The z components do *not* wash out in this picture. Bigger B^0 field scales up the chemical shifts ω, but not the J couplings J_{jk}, so strong magnets take you more to the weak approximation.

If this is not the case, then you keep the full dot product, and Appendix 17.8 page 588 (have not read yet) shows you how you deal with this situation, but I don't the reader is yet ready for this appendix since it mentions things that have not appeared yet such as "rotating frame" frequencies.

This is a secular approximation, and Malcolm clearly states that.

8.7 Heteronuclear spin systems (234). This of course puts you in the situation of "weak coupling" between any pair of different spin types. In this example, I1 and I2 are spins of one type, and S3 and S4 are of another type, so all cross-dot products simplify to z form, but we retain full dots within each group. We still are assuming different chemical shifts within each pair, so we get 8.11.

Now make both pairs chem equiv and assume molecular symmetry as in Fig 8.17 (p 231). In this case, we set certain J's equal and shifts equal and we get Eq 8.12.

Now in addition, make both pairs mag equiv, so we then *drop* the two full dot products and combine other terms to get 8.13.

At this point, author makes this claim without any derivation: if you saturate the two I spins with their Larmor frequency *while* you do your NMR pulse experiment (I call this "blasting"), the claim is that the I spins cannot affect the S spins in any way, so you drop all terms containing I spins and you get 8.14. Moreover, in this situation, the two resulting S spins are mag equiv so you drop their full dot product to get 8.15. In this case, the entire Hamiltonian is treating S3 and S4 as if they were fully non-interacting (isolated) spins, you just have the old $\mu \bullet B$ terms and that's it. This method is called **RF decoupling**. It was mentioned on page 66 as a way to remove unwanted fine splittings in spectra, but no justification was given near page 66 for why it works. Maybe later in the book we shall see, or I will have to look elsewhere.

8.8 Alphabet notation. Several good examples are given here. You represent spins as AB if they are perhaps close in chemical shift, and AX if they are far apart. Spins chem equiv are shown as AA', and spins mag equiv are shown as A^2. The case shown on page 236 shows an AA'BB' which I agree with.

8.9 Topology. Three examples are given of systems with 4 spins. We already dealt with the one on the left. The next one is a $^{13}CH_3$ example! The linear one applies if each spin only sees neighbor J couplings for some reason, molecular shape. I am reminded somehow of dim shadows from the past in the Geoff Chew world.