---------- **Chapter 7: The Nuclear Spin Hamiltonian (170) -------- 52 p ---------- ###**

This is a huge chapter jam-packed with information. Pages 170-222, or 52 pages. Author looks at all the interaction Hamiltonians you can possibly have in an NMR situation, and worries about each in the case of isotropic liquid (gas or liquid), anisotropic liquid, and solid. None of the Hamiltonians is derived in line. The secular approximation is used wherever possible.

7.1 Spin Hamiltonian Hypothesis. The electrons make strong fields at the nucleus, but their motions are "fast" relative to spin motions of the nucleus, so the nucleus sees only an average set of fields. For this reason, it is argued that you can think of H_{spin} all by itself as driving a state time vector as in 7.1.
[Another example of QM system decoupling, like the secular approximation below.]

7.2 EM Interactions. A nucleus can translate and rotate and vibrate I suppose. Probably the hadronics makes the vibrational levels far apart so they don't matter. Translation should not affect anything because it probably averages out in Brownian motion -- otherwise there would be a B field effect perhaps. Well, a nucleus does not "translate" relative to its atom. Nuclear rotation is the NMR stuff. Author breaks down the interaction Hamiltonian into E and B components which are additive. We will look first at E stuff, then at B stuff.

ELECTRIC:

7.2.1 Electric spin Hamiltonian (171). The charge distribution is written in simplified multipole expansion in 7.3, and the effective electric potential is expanded similarly on the next page. Equation (7.3) is a shorthand for the following,

$$\rho(\mathbf{r}) = \Sigma_{\ell m} \rho_{\ell m}(\mathbf{r}) \quad \text{where} \quad \rho_{\ell m}(\mathbf{r}) = f_{\ell m}(r)\, Y_{\ell m}(\theta,\phi)$$

Comment #1: Jackson page 21 (1.53) gives the energy stored in a distribution of potential and charge, where the 1/2 corrects for overcounting. If you were to install a spherical harmonic expansion for $\rho(\mathbf{r})$ and $\Phi(\mathbf{r})$ into Jackson's formula, you would get this result:

$$W = 1/2 \sum_{\ell\, m} \int r^2 dr\ \rho_{\ell m}(r)\, \Phi_{\ell m}(r) \qquad \text{// this is an exact result, I just did it}$$

This is what Levitt means in his (7.4).

Problem: what is the $\ell = 2$ entry in the above sum?

Comment #2: Concerning the nuclear *electric* dipole moment, see physics questions notes. Since a ground state of a nucleus is non-energy-degenerate, and H commutes with P except with perhaps a tiny weak force violation, easy to show that the ground state cannot have an electric dipole moment (because the ground state has a definite parity). The same argument works for all operators that negate under parity, which means $|\ell,m\rangle$ with odd ℓ, so there are no odd multipole nuclear electric moments, as Levitt states top of page 173.

Comment #3: Suppose nuclear spin = 1. Claim is that $\rho_{\ell m}(r) = 0$ for $\ell > 2$. I think the idea here is this: assume the nucleus is in some state |j,m>. What is the expectation value of a space-multipole operator?

$\langle j,m| \; O_{\ell',m'} \; | j,m\rangle$ proportional to Clebsch-Gordon coefficients

If the nuclear ground state has $\ell = 0$, then at most it can have j = s, its spin. Then Wigner-Eckart says you can only have non-vanishing matrix elements for $\ell' = 2s$ and below. Again, having nuclear $\ell > 0$ is not going to happen at low temperature because the hadron levels are so far apart. So this explains the claim made in (7.5). Once again, we have [recall you can do the three Wigner j's in any order]

$s \otimes s = 2s \oplus 2s\text{-}1 \oplus ... \oplus 0$ so ℓ' has to be in this range to get non-vanishing

In particular, if s = 1/2, then you get 0 for $\ell' > 1$. But we already know that $\ell' = 1$ gives 0 (the electric dipole), so only $\ell' = 0$ survives the electric world. Any nucleus with s = 1/2, no matter how complex, acts as a point charge! Non-lumpy. For larger spins, you will need to worry about the quadrupole $\ell' = 2$ moment which can exist and it interacts with $\Phi_{2m}(r)$. As Levitt claims, and as I show in my physics questions notes, you can only have $\Phi_{2m}(r)$ [quadrupole moment] in an electric field that has a *gradient*. Due to the divergence and curl conditions on E, this likely means that the E field has to have a shape like that shown top of page 174, as opposed to a simple 1D linear gradient. [not sure about this]

Note added: In my multipole expansions doc, I show that

$$\phi(\mathbf{R}) = 1 / |\mathbf{r} - \mathbf{R}| = \phi(0) + r_\alpha \partial_\alpha \phi + (1/6) [\, 3 r_\alpha r_\beta - \delta_{\alpha\beta} r^2 \,] \, \partial_\alpha \partial_\beta \phi + \text{octupole and higher terms}$$

and this shows that the Cartesian quadrupole moment term is zero unless you have at least some non-zero second derivatives of the potential, which means at least some first derivatives (gradient) of the E field.

So Levitt's conclusions of this subsection are:

(1) If s = 1/2, then $H_{electric} = 0$

(2) If s > 1/2, then $H_{electric} \approx H_{quadrupole}$ // this book will generally ignore this case it seems

MAGNETIC

7.2.2 Magnetic Spin Interactions. We write down the usual $H_{magnetic} = -\boldsymbol{\mu} \bullet \mathbf{B} = -\gamma \, \mathbf{S} \bullet \mathbf{B}$, spin dotted with the magnetic field. Levitt is strangely silent about the monopole and higher moments. Presumably there can be higher magnetic moments and they will have some fancy interaction with the B field. We will ignore these because of the extreme dominance of the magnetic dipole (and perhaps the general uniformity of the B field). In the electric case we only worry about the quadrupole for $S \geq 1$ because it is then the lowest order non-vanishing interaction!

Comment: We can think of the nucleus as having some $\rho(r)$ charge distribution, and this allows us to work out all the electric multipole moments, I have done this. What is the corresponding quantity to let

you work out the magnetic multipole moments? It must be the current density distribution **J**(**r**) in the nucleus which is a vector quantity. I hunted and I found:

This is all figured out in Raab and deLang and I copied over their results into my multipole document. Yes, there is a magnetic quadrupole interaction and it is given by this classically:

$$H' = - \mathbf{m} * \mathbf{B} - (1/2)\, m_{jk} \nabla_j B_k$$

where

$$\mathbf{m} = (1/2) \int d^3\mathbf{r}\, (\mathbf{r} \times \mathbf{J})$$

$$m_{jk} = (2/3) \int d^3\mathbf{r}\, (\mathbf{r} \times \mathbf{J})_j\, r_k$$ = the magnetic multiple moments of the current distribution

which we can compare to

$$H' = - \mathbf{p} * \mathbf{E} - (1/2)\, q_{jk} \nabla_j E_k$$

where

$$\mathbf{m} = \int d^3\mathbf{r}\, \rho\, \mathbf{r}$$

$$q_{jk} = \int d^3\mathbf{r}\, \rho\, r_j r_k$$

7.3 External and Internal Spin Interactions. Levitt makes an interesting comment here about the relative sizes of internal and external effects. In an IR spectrometer, you have strong local atomic electric fields, and you send in a weak probing light beam to find the spectral lines. The external beam is treated as the small perturbation term forming the interaction Hamiltonian, and it gets out information. In the NMR world, the external field is huge compared to local fields (magnetic) and the smallness of the perturbation Hamiltonian term arises from the smallness of the nuclear spin interactions. So in a sense, these spins are the weak perturbing "probes" used in NMR experiments. You think of the spins as probing the RF pulses you put in with your large magnetic field. Well, a little hazy, but I think I get the point.

EXTERNAL:

7.4 External Magnetic fields. Our RF coil is going to make a B field in the x direction as shown and of course this adds to the big static B field. Since $B = B_z = B^0$ for this, we have $H_j^{static} = -\gamma_j I_{jz} B^0$ where I is the spin and j is for the j^{th} nucleus. They might have different gammas, fine. This is (7.14).

7.4.2. Transverse field. Assume cosine ω_{ref} with phase ϕ_p as shown, we get amplitude B_{RF} as shown, and in the x direction only. Decompose this as on page 179 into the mathematical sum of two rotating B fields so now we have nominal x and y direction fields. We are going to select ω_{ref} (sign and magnitude) so it is close to the Larmor frequency of our spinning moments, and that means one of these

rotating fields will be close to the resonance, and the other will be far away and will have no effect at all, so throw the far away one out. [This is the "rotating wave approximation" RWA in action, see phys quest notes.] The claim is we should keep the first term which is a CCW rotating phasor when ω_{ref} is positive. So we plug in this thing for the B-field into our RF Hamiltonian $-\mu \bullet B = -\gamma I \bullet B$ and since **B** has x and y pieces, we involve the I_x and I_y spin components and boom, we have (7.16). Since Ham is energy, the outside constant of $1/2\gamma B_{RF}$ is an energy, and since h-bar = 1, it is also a frequency called the **nutation** frequency. I don't at this point see the connection between this and spinning top nutation, but the range is supposed to be 1-200KHz. [Well, suppose $\mathbf{B}_{RF} = B\hat{\mathbf{x}}$. We know this makes the I vector "nutate" around the x axis, and this happens at rate $1/2\gamma B_{RF}$ which is much slower than the precession frequency $\omega = -\gamma B_0$. This fast Larmor motion is taken out in the rotating frame, and then you just see the nutation.]

INTERNAL:

7.5 / 7.5.1 Internal Spin Hamiltonian (180). Above we looked at how nuclei interact with externally applied B and E fields. We can generally ignore the E fields for spin-1/2 nuclei. We have already looked at both the external static field, and the probing RF pulse. Now we want to examine how other microscopic things like local electron fields and other spins can affect a spin. For now, we get a list of these things with pictures:

chemical shift = due to B field variation caused by motion of local electrons (not nuclei).

quad coupling = due to E field variations caused by motion of local electrons on spin > 1/2 nuclei

direct dipole-dipole = two mag dipoles affect each other, each makes a B field at the other.

J-couplings = I think this is related to spin-orbit coupling, involves other nuclei AND the electrons

spin-rotation interactions = if the molecule rotates, that can make a B field affecting a spin

All these things are going to cause detail in our FID spectrum, we have already seem some of this in earlier chapters. On page 182 we get a picture suggesting the relative size of these differing effects. The quad is huge, if present, and the dipole-dipole is larger than the chemical shift in general. A good little picture I think.

7.5.2 Simplification of our internal Hamiltonian (183). Recall that the spins "relax" with T1 and T2 times. This is caused by interaction of spins with local stuff, and we are going to ignore these interactions in our Hamiltonian. We are going to do a "secular approximation" to let certain things average out, and we are going to do "motion averaging". I admit, I am confused.

7.6 Motional Averaging (184) // of molecules

Here we first worry about the random *rotation* of molecules in different materials. This is by definition an *intramolecular* effect only. Then we look at random *translation* effects, notion of diffusion and flow, and we are stuck with the diffusion sphere idea for liquids. This is an *intermolecular* effect only. The rest of the chapter worries about the interaction of pairs of spins, and these in general can be both intermolecular

and intramolecular. A counter-example is J-coupling which works through bonds so can only be intra. The spin-rotation case is an oddball that our author gives short shrift at the very end, saying it does not affect NMR much -- it is also just intra.

7.6.1 Modes (184). There are several "modes" of motion: groups rotate on a molecule and vibrate, molecules translate, and molecules rotate.

7.6.2 Molecular rotations (184). Author uses a generic symbol θ to represent the angles needed to describe a molecule's orientation -- a good use of my pseudocode for algorithm description. You start with a Hamiltonian of interest, but then you need to "average it" over a time period that is hopefully $\leq$ the duration of an NMR shot, and then you argue that the averaged Hamiltonian is what counts. This is shown bottom page 184. If $p(\theta)$ describes that angular distribution of your molecules (perhaps they are in an aligning field), then (7.17) shows a "angular average" of your Hamiltonian. The claim is that the time average and the angular average give the same thing. This is the **ergodic hypothesis** used in statistical physics: time average = phase space average. Sounds very reasonable to me.

(1) All gases are isotropic he says. I imagine a strong field might line things up a bit, but I guess that would take a very large field at room temperature (due to spin-lattice type relaxation forces). Isotropic liquids means all molecular angles are equally likely. In this case, $p(\theta) = 1/4\pi$ and you get (7.18) which he calls H^{iso}. Here the time average of the previous page is replaced with an angle average.

(2) Anisotropic liquid might have a director deal, so you cannot then set $p(\theta)$ = constant.

7.6.3 Molecular translations (186). Distinction of **diffusion** and **flow**, maybe two limiting ideas.

(1) In gases, things diffuse a distance larger than your NMR sample size in the experiment time.

(2) In liquids, this is not true, so you define a **diffusion sphere** as shown top page 187 picture

(3) In solids there is **no diffusion** to speak of.

7.6.4. Intra versus Inter molecular spin interactions (187). It is certainly clear what this means. Chart at top of page 188 shows sizes of spin interactions classified intra and inter. The spin-rotation interaction can only be intra, and claim is this is true also for the J-coupling (not clear yet to me -- well, it works through bonds, so can't leave a molecule). In the inter world, you can distinguish for a liquid between short and long range inter effects. Are the two things in the same diffusion sphere or not? Short range interactions are stronger. Not clear to me how this works.

7.6.5. Summary of motional averaging (188)

(1) For **gas**, intra stuff is averages to isotropic, and inter averages to 0, see picture 189. The inter idea here is that every possible orientation of molecule #2 relative to #1 occurs in Δt, so cannot have an average **B** field effect (induced B, that is), for example.

(2) For **isotropic liquid**, where we have that diffusion sphere, short-range inter stuff averages to 0 for the same reason as in a gas. It is a gas within its diffusion sphere, so to speak. The intra is same as gas as well, averages to iso, see 189. Long range inter are "small".

(3) For **anisotropic liquid**, picture is exactly the same as (2) except the intra average is not isotropic.

(4) For most **solids**, the intra-inter distinction is lost and you draw bottom page 191. You cannot do any real simplification, nothing averages to 0 or isotropic.

(5) **Plastic crystals** like adamantine. This is a solid lattice within which molecules can rotate sometimes isotropically with no translation, very cool. $C_{10}H_{16}$ hydrocarbon. The local rotation causes the

intra to average to iso, but since no diffusion, only "long range" inter stuff, in effect, and you have to worry about this. See pictures page 191. Very cool.

7.7 The Chemical Shift (192) // We are now starting into our list shown in (7.5) above

The basic idea is that your applied B field lines up some *electrons*, and they then create a secondary B field which adds to the first, causing the shift. The direction of the induced B field depends on details of your molecule, even at a tiny time instant. Think of the inducer as a electron current ring which may be constrained directionally. [I guess when you say "the electron", you are really thinking about J, the combination of L and S, so electron spin (and its moment) contribute to the B field we are talking about here.] We are talking here of the fact that the total electron wavefunction set (with spins) has a combined dia/paramagnetic magnetization (some complicated 3D function) which is induced by the external B field and which then adds to it, thereby shifting the Larmor frequency. The amount of shift is that the matrix δ is going to tell you.

7.7.1 The Chemical shift tensor δ. The way you handle this kind of situation is to have a 3x3 tensor, as with strain or as with dielectric constant, etc. For the induced field, we write $\mathbf{B}^{\mathtt{induced}} = \boldsymbol{\delta} \bullet \mathbf{B}^{0}$ where δ is as shown page 193. Since B^0 is in the z-direction, we get the second line in (7.21) where only three of the tensor elements appear. Then we put this induced B into our usual $\boldsymbol{\mu}\bullet\mathbf{B}$ Hamiltonian $H = -\gamma \mathbf{I}\bullet\mathbf{B}$ and we can write the induced contribution as in (7.22). Notice now that all three spin components appear, and as usual j tags individual spins of same or different type. Of course δ is a function of generic θ which is the orientation of a molecule at some time instant. [Recall that back on page 56 or so, we talked about chemical shift δ just as a dimensionless measure of the chemical line shift. Probably this is the real δ here that is that shift. Notice here that the δ tensor is dimensionless.]

7.7.2 Secular Approximation (194). I did a lot of work on this, see phys quest notes, and now I understand its general meaning: throw out high frequency components that won't contribute much to your problem's solution, when you are near a resonance. In this context, it means throw out off-diagonal interaction Hamiltonian terms which are non-degenerate. This is explained in Appendix 7.15. So only I_z is diagonal, see Pauli matrices on page 164 top. [Later when there are multiple spins, not so obvious what to do!]

7.7.3 Isotropic Chemical Shift (194). Here we want an angular average of $\delta_{zz}(\theta)$ which appears in (7.23). δ_{zz} tells you how much B field is induced in the z direction by an applied B field in the z direction. If all your molecules were lined up as shown top p 195, then $\langle\delta_{zz}(\theta)\rangle = \delta_{zz}$. But since you have equal amounts lining up in each major direction, so to speak, you get $\langle\delta_{zz}(\theta)\rangle = [\ \delta_{xx} + \delta_{yy} + \delta_{zz}]\ /3$. This is what he means by his good hand-waving argument shown first in the pictures on page 195, then on page 196. My confusion in these pictures was the short white arrow in each. This is the total induced field vector, but we are really only interested in the xx or yy or zz part of that vector in each picture respectively on page 195. This component is the grey vector. In each case, the grey vector lines up with the applied B vector, and this true also on page 196. The answer has to be (7.25) by O(3) symmetry arguments. However, in problem (7.2) you can do a direct but tedious proof. I could solve this problem by rotation group methods and get a fast proof I think, but I know the

answer is right from symmetry. [See phys quest notes for a one line derivation. The angular average of any 3x3 matrix is given by (7.25) !]

7.7.4. Chemically shifted Larmor frequency (196). Our main Hamiltonian is (7.14) on p177, $-\gamma B I_z$. To this we add our chemical shift Hamiltonian (7.24) which is $\gamma B \delta_{iso} I_z$. The sum is written $\omega_0 I_z$ where ω_0 is the new effective Larmor frequency. Remember that this is independent of J, hence of spin S. We get that $\omega_0 = -\gamma B(1+\delta_{iso})$, so we have finally derived the "chemical shift", at least for an isotropic liquid. Of course we don't at this point have any way to compute the 3x3 matrix δ or any of its elements, but I'm sure I could dig up something! It would be a function of detailed molecular chemistry!

7.7.5 Influences on the chemical shift (197). Several qualitative points are made here:

(1) δ is larger in atoms that have lots of states close to the ground state, something I think I could show from general QM arguments. As Z increases, states crouch lower, so get larger δ for larger elements. H has ~10, C has ~200, for example.

(2) If a *nearby* atom has high electronegativity (near atom is O, for example), electrons move away to that neighbor atom, reduce local shielding effect which increases induced fields, increasing δ.

(3) If a molecule has features which cause larger electron-induced B fields (like a benzene ring), these electron fields reduce induced fields (shielding again) and so reduce δ. The electron-ring induced fields will be strong on the ring axis, as shown in the page 197 figure so δ will be low there. But in the plane of the ring, fields are weak, less shielding, higher δ. The point is that the δ your test atom sees depends where it is in a molecule relative to things like benzene rings which create variations in δ. He calls this effect a **ring-current shift**. [more shielding means less δ]

(4) If you have a mixture of two fast-toggling "chemical forms" (isomers) of a molecule, the Larmor line will be at an averaged location. Your response FID will show a single line at the averaged location (not two half-height lines, and not a broadened line). The reason is that the position of the line is (7.27) based on average δ_{iso} which is a measure of the average induced field, and that average is a position, not two positions or a spread in ω-space. By "chemical form" we mean an isomer, not an isotopomer. I wonder why Levitt avoids the word isomer in his book?

(5) If you have a mixture of isotopomers instead of isomers, you get the same average position effect, but the amount of shift is much smaller than for isomers. Don't confuse isomer, isotope, isotopomer, and isotropic, four words meaning different things. We saw the chemical shifts for various isotope atom nuclei on page 62. Remember: the *chemical* shifts are caused by neighboring *electronic* activity. We need an isotope of carbon otherwise it has no net spin.

7.7.6 Anisotropic liquids (198). Things are different because you cannot do the iso average, and you have result shown bottom of page 198 for the δ_{zz} average. Comment that a phase change in liquid can cause a sudden change in $\langle\delta_{zz}\rangle$ as suggested by the pictures here.

7.7.7. Solids (199). Again, cannot do iso average. Top page 200 shows how δ will be different for different crystals in the solid, it if is made into a powder. The claim is that a powder results in a broadened spectrum, not an averaged line position! What is the difference? If the powder granules are large compared to a molecular size, then the local average $<\delta_{zz}>$ is the same for an entire granule. I am not clear on this, but it must have to do with the grain size relative to some other size: molecular, or diffusion sphere or RF wavelength. I suspect Levitt will comment on this at some point. The powder spectrum falls into the area of inhomogeneous broadening. Effect is called **CSA** = chem shift anisotropy.

7.7.8. Summary on chemical shift (200). Picture shows where you go to find formula.

7.8 Electric Quadrupole (201). I went off and did a 3-4 day digression to derive the quadrupole Hamiltonian shown in the appendix page 577. In the usual secular approximation, you then get a Hamiltonian of the form (7.30) where the frequency is given on the next page. This involves the electric field seen by the nucleus, let us not forget.

7.8.1 Isotropic liquid (201) has no average quad nuclear moment since everything bumping around at random, so there is no electric quadrupole activity. [But why doesn't the big external B_0 field tend to line up the nuclear spins, and thus "align the quadrupoles" which you think of as attached to the dipole spin? Well, yes, but in this section of the book we are talking about activities not involving external fields, the "internal interactions". This is I guess the quad of the nucleus interacting with the electric field of the electron wavefunction of the molecule. The nucleus stays put, the molecule rotates randomly, so the electron field is randomized and those $V_{\alpha\beta}$ derivatives maybe average away. In any event, see the following comment.] [The reason for no electric quadrupole in isotropic situation is stated in a different way later, see Section 8.3 notes below.]

Comment: Look at the Hamiltonian (7.30), our secular thing. Consider a vector **a**. The angular average of the component magnitudes must be the same, so $<a_x^2> = <a_y^2> = <a_y^2>$. Therefore, they are each equal to 1/3 a^2. Therefore, $< 3\, I_z^2 - I^2 > = 0$! So <Ham of 7.30> = 0, the claimed isotropic result.

7.8.2 Anisotropic liquid. (202) If things can get lined up, maybe the nuclear quads can line up to some extent [or better to say the molecules get aligned so their electric fields get aligned in a general sense] then $Q \neq 0$ in effect. He is thinking of full bore Q, and then do the average by averaging the gradient. So if you take the average of (7.32'), you must get zero for isotropic.

Comment: OK, here is why $<V_{zz}> = 0$ for isotropic, and this why my $V_{\alpha\beta}$ average away as guessed above. We know that V satisfies Laplace, and we know that all three ∂_i^2 must be equal and therefore equal to 1/3 their sum, but that sum is zero, see comment about vector above! QED.

7.8.3 Solids.(202) Same thing, but now you don't get any averaging of the potential because things are perfectly lined up and don't move.

7.8.4 Electric Quadrupole summary: (202) given by the picture. Fine.

7.9 Direct Dipole-Dipole Coupling (203) (between two nuclear spins). Author shows the right pictures and says this is usually called the **"through space" D-D coupling**. I derive formula (7.34) in my phys quest doc along with (7.35). This last should have $\hbar^2$ if the I's are taken dimensionless. But the H's in this book are in units of ω, not energy, so that is why only one $\hbar$ in (7.35).

The claim is that this effect is really used to determine molecular structure, I would like to see an example of that. You know all the constants, so you are measuring the little distance r between pairs of spins, and I guess each distance is going to show up as a separate line! He will come back to this later.

7.9.1 Secular Dipole-Dipole coupling. (205) [first, original notes as they were] Now suppose we have our strong B field as shown in the picture on page 206. If a spin 1 is aligned along the field, its states $|j_1 m_1>$ will be far apart in energy, but if aligned perp to the field, the states will be arbitrarily close together. You can write the Hamiltonian in terms of raising and lowering operators, but you cannot then throw out off-diagonal terms because they might be close in energy. Therefore, the problem of doing the "secular approximation" on the Hamiltonian we got in the last section is a non-trivial problem. I am not going to track all this down today, but I will try to understand the implications of the results.

First, suppose the two interacting spins are coming from the same type of atoms (same isotopes and same atoms), then the secular result is shown page 206. Somehow we pick up an *overall* angle factor as shown and the rest of the Hamiltonian is simplified as shown. It is very unobvious to me how this has happened. The angle factor is the angle between B^0 and the line between the pair of spins.

Second, suppose the spins are different (different isotopes or atoms or both). In this case, we only keep the z-terms in the dot product and this lowers the 3 to a 2, and we get the result shown top of page 207. In both cases, we have the same angle factor. If you could somehow make all interspin axes line up at the magic angle (there are two), then the coupling goes completely away! You might be able to do this in a crystal by tilting the sample? The magic angle has nothing to do with the direction of the spin vectors themselves, it is the axis between the spins versus the B field. Very strange.

[now, notes added 2.3.08.] First of all, looking at (7.34), if we are allowed to "keep only I_z terms", the first term becomes $3(I_{1z}e_z)(I_{2z}e_z) = 3e_z^2\, I_{1z}I_{2z}$. Then adding the two terms gives $(1/2)(3e_z^2 - 1)2I_{1z}I_{2z}$ and this gives result (7.39) and, since $e_z = \cos\theta$, this explains where the angular factor comes from in this case as in (7.37). In the more general secular approx, we have to also keep terms like $I_1^+ I_{2z}$ since these imply energies close to the z-only terms. If you maintain all such terms, you do in fact get the result (7.36) which has the same angular factor, as a simple calculation shows. At first this seems rather amazing, but as shown in writeup **"secular dipole dipole.doc"**, there is a reason for this. Write $H = [3e_i e_j - \delta_{ij}]\, I_{1i}I_{2j}$ for (7.34), see this as the contraction of two symmetric rank-2 tensors. Put into sphericals, the left tensor has only a j=2 component, so the contraction picks out the j=2 component of the right tensor, so then $H = \Sigma_m\ (-1)^m\, A_{2,m}\, B_{2,-m}$ where A and B are the spherical j=2 tensors. But, only the $B_{2,0}$ combination of $I_{1i}I_{2j}$ has $M_z = 0$ so this term contains all the $I_{z1}I_{z2}$ and $I_1^+ I_2^-$ type terms that we want to keep for secular. Thus, the secular answer is just $H = A_{2,0}B_{2,0}$ which is the product of the m=0 components of two spherical quadrupole objects. The $A_{2,m}$ tensor for $\hat{e} = \hat{e}(\theta,\phi)$ is really $Y_{2,m}(\theta,\phi)$ [we ignore constants here] so the angular factor

$(1/2)(3\cos^2\theta - 1)$ is recognized as $Y_{2,0}(\theta,\phi)$. In the homonuclear case, we need to keep the $I_{1z}{}^{+}I_{2z}{}^{-}$ terms, but we can throw them out in the heteronuclear case, hence (7.36) and (7.39).

7.9.2 Isotropic liquids. (207) The angle factor averages to 0 to the DD coupling goes away.

Comment: What does this magic angle imply? If you have an AX chemical bond in a molecule and if that bond is oriented at the magic angle relative to B, $H^{DD} = 0$ and whatever effect the DD coupling was having on your NMR spectrum at other angles goes completely away. But at this point in the book, we don't know much about such spectra, so this section is just being put into the knowledge bank for later use in the book.

7.9.3 Anisotropic liquids. (208) Now the angle factor has some average, as shown

7.9.4. Solids. (209) Here for a crystal structure you have a 3D array of coupled spins as shown top page 210. If the sites are allowed to rotate freely as in plastic crystals (adamantane), then intra goes away, just as it does in an isotropic liquid. Otherwise you have to use the general case Hamiltonian.

7.9.5 (210) Summary for Secular dipole-dipole. Authors draws his usual graph, I like it.

7.10. The J Coupling. (211) A different animal. This is an interaction between two spins which is indirect, propagating not "through space" but rather through an electron orbital that is making a bond between two atoms having nuclear spins. See explanation below of this idea. This coupling can even work through a sequence of bonds, and we use the name ^2J if it is working through 2 bonds, for example. So chemical shift tells you about the shielding of your local environment, helping you to know what chemical group your spin is sitting in, while the J coupling tells you something about the electron bonds going to the atom in which a nuclear spin is located. A whole new world of information.

Obviously there is no component of the J coupling between separate molecules, so inter = 0.

The Hamiltonian is given in a highly compact form top of page 212 where we have a 3x3 J coupling tensor linking our two spins. How would I "derive" this form of the interaction Hamiltonian? Probably this is the most general form you can write that is linear in each spin vector, and we expect linearity just on the basis that a spin I makes a field B proportional to I which causes a distant splitting proportional to B. For now, that is good enough for me.

7.10.1 Isotropic situation. (212) We have $\mathbf{I_1} \bullet J \bullet \mathbf{I_2}$ as our Hamiltonian for a molecule containing two spins where J is our 3x3 matrix thing. Imagine we are doing a temporal average and the spin directions don't change, but the molecule orientations are random. Then the average of the above is $\mathbf{I_1} \bullet \langle J \rangle \bullet \mathbf{I_2}$. But from my phys quest notes, I know that $\langle J \rangle = \alpha I$ where α is 1/3 the sum of the diagonal elements of J. Thus, the result is $H = \alpha\, \mathbf{I_1} \bullet \mathbf{I_2}$, and this agrees with (7.47) + (7.48). If the spins are different type, then you can throw out raising and lowering operators and you get the secular result $H = \alpha\, I_{1z}\, I_{2z}$ as shown in (7.50). If the spins are the same type, you cannot do this approximation (heteronuclear case).

Now he gives some ballpark estimates of coupling sizes in Hz (this whole book I now realize is trying to show Hamiltonian in ω units, except in this case it uses Hz units by tradition.)

^3J might be only 7 Hz ! ^1J might be 50-150 Hz.

In a ^{2}J case with spin on X, the coupling is a function of the angle of the X-Y-X bond. So by measuring the Hz, you can deduce this angle! Similarly, in the picture shown page 214, you have a ^{3}J situation between two H spins in a peptide bond. The claim is that you can use NMR data to somehow figure out the torsional angle at each peptide bond of a protein. The picture shows how the NMR J-coupling in Hz should vary with the angle, called a **Karplus relationship** curve. The different black dots in the plot are the spins of different H pairs in many peptide links of a protein. From the location of the dots, you know the distribution of angles, but I don't think you know which angle goes where. I can imagine a lot can be done with this idea. Secondary protein structure using NMR. [I think this was mentioned in one of my two bio books, alternative to crystal x-ray]

7.10.2. Non-isotropic (including solids). (214) Here you have to use the full Hamiltonian top page 212, and it includes the isotropic component already noted plus the "J anisotropy" which is the rest. Author has nothing to say about this class of NMR.

7.10.3 Mechanism of the J coupling. (215) In regular dipole coupling "through space", the levels of a spin are split due to the B field of the other spin. Here, the levels of a spin are split by a local B field caused in effect by the other spin and *propagated through* a chemical bond orbital. The words and picture here try to give an arm-waving argument to explain the cause of the splitting. The bond contains an electron pair with opposite spins it is assumed. If the nuclear spins are opposed, if the up electron is on the up spin atom (and down on down), you get a lower energy state than the opposite case. So as one of the spins jumps between its quantum states, the size of the jump is affected by the other spin. I wonder how you make an RF pulse at 7 Hz ?

7.10.4 J coupling summary. **(216)** Another summary tree picture. Note that inter = 0 for J coupling.

7.11 Spin-Rotation interaction. (216) As nuclear + and electron - charges rotate when a molecule rotates, they make B fields which affect the nuclear spin. This mechanism I think acts in the reverse direction to produce thermal equilibrium spin distributions we read about earlier (relaxation). The claim is that this interaction does not enter NMR spectra, except in certain cases. Author has elected to omit this from his general list, so we don't get any Hamiltonians here. Just an added section.

7.12 Summary of all interaction Hamiltonians in this chapter. (217) At the left are the external guys, caused by the B field and the RF pulses. Then on the right are all the internal things we have been reading about, such as the dipole-dipole, the J coupling, and the chemical shift. The quad electric effect is only present with certain nuclei as we know, spin > 1/2. When present, it is large in solids.

Summary of the results of this chapter:

External E and B fields:

- Magnetic: $H^{mag} = -\boldsymbol{\mu}\bullet\mathbf{B} = -\gamma \mathbf{I}\bullet\mathbf{B} = -\gamma B^0 I_z$ from static external field
  $H' = -\gamma B_{RF} I_x \approx -1/2\ \gamma B_{RF} [\cos(\omega_{ref} t + \phi_p) I_x + \sin(\omega_{ref} t + \phi_p) I_y]$ from pulse, p 179

- Electric: $H^{elec} = 0$ unless spin ≥ 1, then $H^{elec} = -(1/2)\ q_{ij} \nabla_i E_j$ from quadrupole

Comment: The book implies that even for $I \geq 1$, $q_{ij}\nabla_i E_j \sim 0$ so we never worry about this interaction with an *external* electric field, whether static or part of the RF pulse. However, the quadrupole can be large due to *internal* electric fields created by the electron clouds. Hard to make a strong E field gradient with a distant external apparatus, but local electron cloud could do it easily.

Internal interactions:
Motional averaging:
intermolecular: gas = 0, iso liquid = long only, other = long + short
intramolecular: always something

Chemical shift: $H^{cs} = -\gamma \delta_{zz}(\theta) B^0 I_z$ // secular. For iso get δ^{iso} in there.
inter = 0 for gas, = long only for iso liquid, = tiny long for aniso liquid

Chemical shift + External Mag: $H = -\gamma B^0 I_z - \gamma \delta_{zz}(\theta) B^0 I_z = -\gamma B^0 (1 + \delta) I_z = -\gamma \omega^0 I_z$

Electric quadrupole: $= \omega^Q (3I_z^2 - I^2)$ secular, where $\omega^Q = Q\langle V_{zz}(\theta)\rangle/[4I(2I-1)]$ p 202, = 0 for iso

Dipole-dipole $H = b_{12} (3\, \mathbf{I_1 \bullet n}\, \mathbf{I_2 \bullet n} - \mathbf{I_1 \bullet I_2})$ where $b_{12} = \gamma_1\gamma_2\hbar/[4\pi r_{12}^3]$ p 204
$= d_{12}(\theta) (3\, I_{1z} I_{2z} - \mathbf{I_1 \bullet I_2})$ where $d_{12}(\theta) = b_{12}(3\cos^2\theta - 1)/2$ secular, p 206
except the $\mathbf{I_1 \bullet I_2}$ term vanishes secular if nuclei are different
for iso in general, or at magic angle θ_{magic}, we get H = 0 intra.
inter = tiny long only in liquid

J coupling $H = 2\pi\, \mathbf{I_1 \bullet J \bullet I_2}$ p 212; for iso this is $H = 2\pi\, J_{12}\, \mathbf{I_1 \bullet I_2}$ with J_{12} = usual average
which then becomes $2\pi\, J_{12} I_{1z} I_{2z}$ for iso with different nuclei
inter = 0

So, for isotropic liquids, what do you get from the above? If we ignore the inter long part, then
chem shift = $-\gamma\, \delta_{iso}\, B^0\, I_z$, dipole-dipole = 0, J coupling = $2\pi\, J_{12}\, \mathbf{I_1 \bullet I_2}$ for same nuclei.