********** Part 4: Uncoupled Spins-1/2 **********

---------- **Chapter 9: Single Spin-1/2 (241-271) -------- 30 p ---------- ###**

9.1 The Zeeman eigenstates (241). We represent the spinor states for the J = 1/2 representation of the rotation group as if they were vectors for the J = 1 representation, which of course is going to cause interpretation problems. The "Zeeman effect" (1896) is the splitting of an electronic state into two states in a constant B field, due to the $H = -\mu \bullet B$ Hamiltonian. The "Stark effect" (1913) is the similar thing in an electric field.

Comment added: the arrows are really $\langle\alpha|\mathbf{I}|\alpha\rangle$ and $\langle\beta|\mathbf{I}|\beta\rangle$. The arrows don't represent the states α and β as he says, they represent the expectation value of the spin operator in states α and β.

9.2 Quantum indeterminacy. (242). I am totally familiar with this notion.

9.3 Energy levels (243). This arises from $H = -\mu \bullet B = -\gamma I \bullet B = -\gamma I_z B_z = +\omega^0 I_z$ where $\omega^0 = -\gamma B_z$. We always think of $B_z > 0$. Suppose it happens that $\gamma < 0$, so that $\omega^0 > 0$. Then the +1/2 spin state would be the upper state, the normal way we would draw things. But the more common situation is that $\gamma > 0$ so that $\omega^0 < 0$ and this makes the +1/2 spin state be the lower state as shown in the picture. This is the more common situation in NMR so I guess that is why Malcolm draws it this way.

9.4 Superposition States (244)

9.4.1 General spin states (244). Just fine.

9.4.2 Vector notation (245). Just fine.

9.4.3 Some particular state (245). Using the Pauli matrices from page 164, Malcolm shows a state that must be the +x state since it is a + eigenstate of I_x. He identifies next the -y state. On page 247 he writes 6 states for the various directions. Remember, it is only the phase between the two components that matters for the non-z eigenstates. He then writes an expression for what I might call not I_z but $I_{\theta,\phi}$ or $I_{z'}$ where z' has been rotated θ and ϕ, then the eigenstate is as shown. This would be easy to verify, fine.

9.4.4 Phase factors (248). They don't affect the eigenstateness of an eigenstate.

9.5 Spin Precession. We consider a positive forward increment in time τ. Then (9.10) shows from the SE how any state moves in time, just the usual j = 1/2 rotation matrix around z by angle $\omega^0\tau$ where ω^0 is not some arbitrary number, it is the energy split between our two states in units of $\hbar$. That is to say once again, a state propagates by application of $R_z(+\omega^0\tau) = \exp(-i\omega^0\tau I_z)$. It is this way because the external B field is in the z direction.

9.5.1 Dynamics of the eigenstates (249). First example: assume $\gamma > 0$ so $\omega^0 < 0$. Then assume τ such that we rotate by amount $\pi/2$, so that $\omega^0\tau = -\pi/2$. Compute action of this on the +z state. We just pick up a phase.

9.5.2 Dynamics of superposition states (251). By such states he means states other than the two eigenstates of I_z. Example: apply our same $R_z(-\pi/2)$ operator to the +x state. As expected, it rotates negative right hand rule to the -y state. And so on, as shown in the picture bottom page 251. The upshot is this: If you start in the +x state, your arrow is going to "precess" clockwise in the x-y plane. There is as yet no applied "force" except the static B field. It seems pretty clear that if you start a vector anywhere in the x,y plane, it will rotate in this manner.

Well, as shown page 250 middle, the R_z matrix is diagonal in the z representation, and it rotates the upper component of a spinor one way, and the lower component the other way. This is why it is more than just a phase except for the two eigenstates.

So far, we have not looked at the effect on a spinor vector that starts at an arbitrary location in our vector picture. He has avoided that issue so far. He has commented that cone pictures "don't work", I am not sure why that is the case, they seem pretty useful to me for showing indeterminacy in the other two directions, like the electron orbital pictures.

9.6 Rotating frame (252). In picture on 253 we define a rotating frame with primes and Φ is shown as a positive angle and $\Phi = \omega_{ref}t + \phi_{ref}$. Yes, normally $\omega_{ref} < 0$ for $\gamma > 0$, but for now think of $\Phi > 0$. Now, equation 9.a simply defines state +x' as positive rotated +x state, no fancy frames yet. But if we were riding in the rotating frame, we would say $+x'_{rot} = +x$ as stated in 9.b (from our point of view). These two equations then give 9.c which leads us to define our rotating frame states (with twiddle) as shown in 9.13, all fine by me. The rest of this page computes what the SE looks like in the rotating frame. The result is as expected, but the rotating-frame Hamiltonian picks up an extra "Coriolis force" term as shown in 9.16. Notice the sign sense of the rotated H operator. We are not surprised to find an extra term in our non-inertial frame of reference.

9.7 Precession in a rotating frame (256). The Hamiltonian *in the rotating frame* (rotating at ω_{ref}) has the trivial form shown in 9.18 and 9.19. It is just a frequency shift, as we perhaps would expect. We see our old friend Ω_0 showing up now as the Larmor frequency as measured from ω_{ref}.

We now define δ_{ref} according to 9.20 as that which goes with ω_{ref} . We know that the full δ goes with ω^0 , and we end up then with 9.21. The dimensionless chemical shift off δ_{ref} is proportional to Ω_0. I agree with the picture shown at the bottom, with the δ arrow going to the left and the Ω going to the right, for cases in which $\gamma > 0$. I think the rotation sense arrows are wrong, but I will review that at some future time, don't think it matters much. The page 258 picture is then for $\gamma < 0$ and now he draws BOTH δ and Ω axes to the left, which does seem odd to me, but it is historical convention I think.

Now, if we are in this rotating frame and if $\delta = \delta_{ref}$ so we are right on resonance with ω_{ref} (our frame rotation rate), then the spin does not precess at all, it appears to be fixed -- frozen!

9.8 RF pulse (258). Now we make this connection: we are going to apply an RF pulse at frequency ω_{ref} and we are going to then take that as the speed of our rotating frame. Up to now, ω_{ref} was just "some number".

9.8.1 Rotating Frame Hamiltonian (258). We now have an extra RF term in the Hamiltonian. First, we assume it is a plane wave in the lab x direction, but we do the sum and difference trick then throw out the difference since far from resonance, and we end up with 9.22 as expression for our RF-only Hamiltonian piece in the lab frame. It is a mixture of I_x and I_y, and it moves in time. At page top we include this piece and the original static-B-field piece, everything in lab frame. If we transform this complete H to the rotating frame, we get 9.24 + 9.25. We have used the phase convention of 9.17 page 256 (for the two sign of γ cases) so that the resulting equation is true for either sign of γ and the ω_{nut} is always positive.

Now let's look back more carefully. We assumed the RF field had phase ϕ_p, while our rotating reference frame had phase ϕ_{ref}. Only the ϕ_p ends up in our result 9.24, and variable t does not appear at all, so in the rotating frame, our H_{RF} is constant in time. If we write out the rotation, we end up with 9.26 as our final result: $H_{rotating\ frame} = \Omega^0 I_z + \omega_{nut} (\cos\phi_p I_x + \sin\phi_p I_y)$ and $\omega_{nut} = | 1/2\ \gamma\ B_{RF} |$.

So what are we going to do with this "big result" ? We need to do some examples.

Commented added 1.24.08. I fuzzed this point. The RF pulse is *always* applied in the $\hat{x}$ direction only. However, by adjusting the phase ϕ_p of this pulse at the exact instant that you turn it on, you can in effect "simulate" producing an RF pulse in directions other than the $\hat{x}$ direction always with phase 0. The way this works is shown page 259. You add and subtract the sine I_y term :

$H_{RF} = -\gamma B_{RF} \cos(t\omega_{ref}+\phi_p)\ I_x$ in reality, but write this as

$$= -(1/2)\gamma B_{RF} [\ \cos(t\omega_{ref}+\phi_p)\ I_x + \sin(t\omega_{ref}+\phi_p)\ I_y\ ] \quad ***$$
$$-(1/2)\gamma B_{RF} [\ \cos(t\omega_{ref}+\phi_p)\ I_x - \sin(t\omega_{ref}+\phi_p)\ I_y\ ]$$

You can regard this as the RF field you are applying. The second term "rotates the wrong way" relative to the Larmoring spins and has no effect so you just ignore it, and that leaves you with the first term which rotates in the "right way". Regardless of the value of ϕ_p, the expectation value of H_{RF} describes a transverse excitation magnetization that rotates near the Larmor frequency. So disabuse yourself of the notion that a $(\beta)_\phi$ pulse involves changing the RF field in the apparatus from the x direction to some ϕ direction by rotating the excitation coil or some such nonsense.

However, in a *thought* experiment, you could do a $(\pi/2)_y$ pulse either by setting the phase $\phi_p = \pi/2$, or you could actually rotate the excitation coil to supply B_{RF} in the $+\hat{y}$ direction with $\phi_p = 0$. Let's pursue this idea a bit. In our primed thought experiment we do this:

$H_{RF}' = -\gamma B_{RF} \cos(t\omega_{ref}+\phi_p')\ I_y$ in reality, but write this as

$$= -(1/2)\gamma B_{RF} [\ \cos(t\omega_{ref}+\phi_p')\ I_y + \sin(t\omega_{ref}+\phi_p')\ I_x\ ]$$
$$-(1/2)\gamma B_{RF} [\ \cos(t\omega_{ref}+\phi_p')\ I_y - \sin(t\omega_{ref}+\phi_p')\ I_x\ ]$$

Now suppose we make a guess and we set $\phi_p' = \phi_p + 3\pi/2$. We can then look up these facts:

$$\cos(t\omega_{ref}+\phi_p') = \cos(t\omega_{ref}+\phi_p + 270) \rightarrow + \sin(t\omega_{ref}+\phi_p)$$
$$\sin(t\omega_{ref}+\phi_p') = \sin(t\omega_{ref}+\phi_p + 270) \rightarrow - \cos(t\omega_{ref}+\phi_p) \quad \text{checked}$$

giving us

$$H_{RF}' = -\gamma B_{RF} \cos(\omega_{ref}+\phi_p')t\, I_y \qquad \text{in reality, but write this as}$$

$$= -(1/2)\gamma B_{RF} [\ \sin(t\omega_{ref}+\phi_p)\, I_y - \cos(t\omega_{ref}+\phi_p)\, I_x\ ]$$
$$-(1/2)\gamma B_{RF} [\ \sin(t\omega_{ref}+\phi_p)\, I_y + \cos(t\omega_{ref}+\phi_p)\, I_x\ ]$$

$$= +(1/2)\gamma B_{RF} [\ \cos(t\omega_{ref}+\phi_p)\, I_x - \sin(t\omega_{ref}+\phi_p)\, I_y\ ]$$
$$-(1/2)\gamma B_{RF} [\ \cos(t\omega_{ref}+\phi_p)\, I_x + \sin(t\omega_{ref}+\phi_p)\, I_y\ ] \ ***$$

which we can compare to our original x direction result

$$H_{RF} = -(1/2)\gamma B_{RF} [\ \cos(t\omega_{ref}+\phi_p)\, I_x + \sin(t\omega_{ref}+\phi_p)\, I_y\ ] \quad ***$$
$$-(1/2)\gamma B_{RF} [\ \cos(t\omega_{ref}+\phi_p)\, I_x - \sin(t\omega_{ref}+\phi_p)\, I_y\ ]$$

The term that goes in the "right direction" is the same in either case meaning that if we keep only the correctly rotating term, we get $H_{RF}' = H_{RF}$. So these two pulse applications should be equivalent.

Conclusion: These two situations provide the same excitation:

RF in $\hat{x}$ phase = ϕ_p
RF in $\hat{y}$ phase = $\phi_p' = \phi_p + 3\pi/2 = \phi_p - \pi/2$.

Suppose you were to do a pulse $(\beta)_{-y}$ with RF = $\hat{x}$. This pulse has $\phi_p = -\pi/2$. This would be equivalent to doing a pulse in the $\hat{y}$ lab with $\phi_p' = \phi_p - \pi/2 = -\pi$ which is then $(\beta)_{-x}$. [I may have made a goof in this last section, but don't need the results of this "thought experiment".]

9.8.2 The x-Pulse (260). I think we have to consider ω_{ref} and ϕ_p as applying both to our mathematical rotating frame and to the applied RF pulse [unsure] . So let's do an x direction pulse as we set up in the last section, but we assume $\phi_p = 0$ and go right at resonance. Then $H_{rotating\ frame} = \omega_{nut} I_x$. Earlier on page 249 we saw how we can move any state in time by applying the exponentiated Hamiltonian, for example 9.8. Here, however, we have I_x instead of I_z, so the time driver is as shown in 9.27 with $\beta_p = \omega_{nut}\tau_p$ where τ_p is the duration you choose for your pulse. Appendix 17.3 proves that our Hamiltonian driver is 9.30, an x rotation in the z basis. Now suppose we arrange B_{RF} and τ_p such that $\beta_p = \omega_{nut}\tau_p = \pi/2$. Then we find that our pulse rotates our +z state into the -y state as shown in the picture page 261. It turns out you can always use these pictures to see what a rotation does to our spin represented as a vector. We always ignore phases. He says "do you get the idea? ". So, this first pulse example is called $(\pi/2)_x$. The **"flip angle"** is $\pi/2$, being β_p. If you do a **π_x pulse**, you flip your +z state to the -z state as shown mid page 262. And of course a ± x state is only going to change by a phase.

So the point is this: if you know where your spins are in equilibrium, you can perhaps design RF pulses to cause the spins to flip in a certain way. For example, if all spins were in the +z direction (perhaps in TE at K=0), then a $(\pi/2)_{\mathbf{x}}$ pulse would put all spins into the -y state! Of course we are going to have to work the thermal issue into this later.

9.8.3. Nutation (263). In the rotating frame, with an RF field applied, our states behave in a simple manner. If we had a +z state, it just rotates "slowly" around the x axis as shown bottom page 261. If we have a very long RF pulse, this vector just rotates at the slow nutation frequency. This was a state vector in the rotating reference frame. If we go back to the lab frame, of course the dominant z rotation reappears and we get the state motion as shown page 263. We get this spiral motion with very fine threads. With the spinning top, the bounce of the path of the tip was called nutation. I don't think the analogy is very apt because here the nutation frequency is slower than the high speed rotation in z. The top's nutation is slow compared to the top rotation, but with the top we also have the precession rate which is a third thing which we don't have here. And the nutation is faster than the precession I think. But OK, it is just a name. I can easily visualize the situation in either lab or rotating frame.

Again, so far we have been exactly on resonance with our RF pulse to get the behavior just described.

9.8.4. Pulse of general phase (263). We are still on resonance, so we have a general mix of just Ix and $I_{\mathbf{y}}$ as shown, ie, we no longer say $\phi_{\mathbf{p}} = 0$. The rotation "propagator" is then shown above 9.32 where as usual you just stuff the Hamiltonian into the exponent of e to see what happens to a state over time. We are always in the rotating frame picture, and time is inside $\beta_{\mathbf{p}} = \omega_{\mathbf{nut}}\tau_{\mathbf{p}}$. In effect, you are now rotating the spin vector about a "rotation axis" which is in the x-y plane but rotated $\phi_{\mathbf{p}}$ away from the x axis. The Euler interpretation of the product of the three rotations works fine. The explicit matrix for our propagator is shown 9.33 which seems right to me. So when $\phi_{\mathbf{p}} = 0$, we are talking rotation axis = x. When $\phi_{\mathbf{p}} = \pi/2$, the rotation axis is the y axis. They use x-bar for $\phi_{\mathbf{p}} = \pi$.

9.8.5. Off-resonance effects (265). Now we maintain the first term in our rotated-frame Hamiltonian. We now have a linear combination of all three spin operators. This linear combination can be written in terms of a new angle $\theta_{\mathbf{p}}$ being a usual polar angle, so 9.34 is obvious, and the dot product $\boldsymbol{\omega}_{\mathbf{eff}} \bullet \mathbf{I}$ is just another way to write what appears on page 265 [think $\hat{\mathbf{n}} = \boldsymbol{\omega}_{\mathbf{eff}}/\omega_{\mathbf{eff}}$]. Here Malcolm is putting primes on things to remind us that we are always in the rotating frame. The Hamiltonian can be written as the set of 5 rotations shown top page 267. You then exponentiate this in the usual way to make states "move" in Schrodinger picture (but rotating frame). The exponentiation has the usual "annihilating rotations" and telescopes. Easier to use the Euler angle argument for 9.37: back rotate to the z axis, rotate by $\omega_{\mathbf{eff}}\tau_{\mathbf{p}}$, then forward rotate back, and you have accomplished a rotation about that $\boldsymbol{\omega}_{\mathbf{eff}}$ axis at θ,ϕ.

So 9.37 shows how a state moves in time (still in the rotating system). I think the rotating frame is still rotating at $\omega_{\mathbf{ref}}$. So now we study the pictures on page 267 carefully. If $\Omega/\omega_{\mathbf{nut}}$ is large positive, then angle θ is small and we are close to just doing a normal z rotation. Our spin rotation axis is almost +z, so almost rotating our spin vector around the z axis. The path of the tip of the spin "polarization" is shown, it is a small loop not centered on the +z, but centered on the white arrow. I think the pictures are all shown for $\phi_{\mathbf{p}} = 0$. Then the picture with $\theta_{\mathbf{p}} = \pi/2$ is the one with $\Omega = 0$ and

we are just rotating around the x axis as in our on-resonance case with zero phase, as shown on page 260.

Now, it seems pretty clear that if you are trying to move your spin polarization from +z to -z, the picture marked ratio +4 or -4 has a low probability, whereas that with 0 has a high probability. In the ±4 cases, the rotation axis just is not going to get you to the other z-direction. This then is what the picture on page 268 is showing. As you move away from resonance, your probability for flipping drops off. The picture is shown assuming the pulse has a duration that makes the on-resonant case flip, which means we have $\omega_{nut}\tau_p = \pi$ for our pulse length. I would like to know the equation for this curve. It is going to be this:

$$|\langle\beta|\ R_y\ (\theta)\ R_z(\omega_{eff}\tau_p)R_y\ (-\theta)\ |\ \alpha\rangle|^2$$

But look now page 264 result (9.32) and (9.33). We know the above result in the z-x-z case, but we want it in the y-z-y case. When I use page 577 for the 2x2 matrices calling the middle argument β, I get a 2x2 matrix which have this:

$$\text{upper left component} = e^{-i\beta/2}\, C_{\theta/2}{}^2 - e^{+i\beta/2}\, S_{\theta/2}{}^2$$

$$\text{lower right component} = e^{-i\beta/2}\, S_{\theta/2}{}^2 + e^{+i\beta/2}\, C_{\theta/2}{}^2$$

$$\text{both diagonal elements} = -2i\, S_{\theta/2}C_{\theta/2}S_{\beta/2} = -i\, S_\theta S_{\beta/2}$$

If I put this between a + and - state, I pick off just this diagonal element. So that suggests that

$$|\langle\beta|\ R_y\ (\theta)\ R_z(\omega_{eff}\tau_p)R_y\ (-\theta)\ |\ \alpha\rangle|^2 = S_\theta{}^2 S_{\beta/2}{}^2 \text{ where } \beta = \omega_{eff}\tau_p \text{ and } \tan\theta = \omega/\Omega\ .$$

where ω is the nutation frequency. So if we plot the above probability against θ, it is a simple $\sin^2(\theta)$ plot which peaks at $\theta = \pi/2$ which puts our spin axis in the x-y plane. If $\beta = \pi$ for a full flip, then $S_{\beta/2}{}^2 = 1$ as well. So we need to convert this to Ω using $1/S^2 = 1 + 1/\tan^2$ so $S_\theta{}^2 = \tan^2 / (\tan^2 + 1) = (\omega/\Omega)^2 / (\omega/\Omega)^2 + 1) = 1 / [\ 1 + (\Omega/\omega)^2\ ]$ so my claim is that the above probability is

$$|\langle\beta|\ R_y\ (\theta)\ R_z(\omega_{eff}\tau_p)R_y\ (-\theta)\ |\ \alpha\rangle|^2 = 1 / [\ 1 + (\Omega/\omega)^2\ ]\ S_{\beta/2}{}^2$$

But this other sine is $\sin^2\ (\omega_{eff}\tau_p/2) = \sin^2\ (\ \sqrt{\omega^2 + \Omega^2}\ \tau_p/2\ )$ so it also has Ω dependence. The pulse length is set such that this peaks at 1 for $\Omega = 0$ (our π pulse), but then this thing oscillates as Ω grows either way, symmetrically, and $\sin^2$ is always positive. So this I think is the plot of the lower graph!

$$|\langle\beta|\ R_y\ (\theta)\ R_z(\omega_{eff}\tau_p)R_y\ (-\theta)\ |\ \alpha\rangle|^2 = \sin^2\ (\ \sqrt{\omega^2 + \Omega^2}\ \tau_p/2\ )\ /\ [\ 1 + (\Omega/\omega)^2\ ]$$

The envelope drops as $1/\Omega^2$ for large Ω. Now, the envelope drops to half height at $\Omega = \omega = \omega_{nut}$ so that is why he says "the bandwidth of the pulse is proportional to ω_{nut} [I would say ω_{nut} was the half width at half height]. So, if you want a broad pulse in the lower picture on page 268, perhaps to

cover a large range of chemical shifts, then you need to make ω_{nut} be large, which means make B_{RF} be large! When you do this, generally you don't reach "other isotope spins", so you need a separate system for each isotope you want to look at. Max practical ω_{nut} is 200 KHz he says.

Comment: Now I have to put some pieces together. The curve shown bottom of page 268 shows the ability of a single RF π-pulse to flip all the spins backwards against the static B field. If you do such a flip, the spins are going to spontaneously flip back to static B alignment, modulo thermal, and radiate, making the FID pulse we haven't studied yet, and which we are going to Fourier analyze. So you have to make sure you have enough bandwidth to pick up all your chemical shifts of interest, or there will be no power in the radiated field and doing a Fourier cannot create something from nothing!

Author goes on to say on page 269 that we have assumed a perfect square pulse. If we shape this thing, we know that is also going to add to its bandwidth. You could vary both the amplitude and the frequency (chirp) if you wanted, but Levitt does not go into these details.